SYNTHESIS AND CHARACTERISATION OF METAL ORGANIC FRAMEWORK BASED ON 3d AND 4f METALS

Summary of Work (5000 Words)

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I have divided my thesis into four chapters as the following:

Chapter 1: Unveiling role of metal centres [Co(II) and Ni(II)] in mononuclear metal complexes towards chemodosimetric detection of sulfide from purely aqueous medium: Experimental and DFT corroboration with real field application.

Chapter 2: Exploratory studies on azido-bridged pincer metal [(Ni(II) and Mn(II)] clusters as ditopic colorimetric chemosensor for S^{2-} and Ag^{+}: combined experimental and theoretical outcome with real field application.

Chapter 3: 3d -4f Single molecular magnet with considerable anisotropy of magnetisation having low spin Fe(III) in Fe_4-Ln_2 (Ln = Dy(III), Tb(III) and Er(III)) Complexes.

Chapter 4: An unprecedented penta coordinated azido Zn complexes derived from N,N,O-donor clickable ligand with its application in sensing hazardous analytes S^{2-} and Ag^{+}.

Chapter 5: Pyrazine assisted dimerization of oxo-bridged Schiff base Cu(II) complex.

Chapter 6: Scope of the thesis and final conclusion.

Chapter 1

Unveiling role of metal centres [Co(II) and Ni(II)] in mononuclear metal complexes towards chemodosimetric detection of sulfide from purely aqueous medium: Experimental and DFT corroboration with real field application

Introduction:

The Chemistry of Coordination complex has started since the 19th century with the discovery of Werner's theory. Throughout the century, the development and the research in this field is still ongoing due to the vast application [1] of Coordination complex in the field of catalysis, drug delivery, medicinal chemistry [2], gas adsorption, sensing [3], magnetism and so on. In the last decades, vast numbers of organic compounds have been reported to sense the particular metal ions or analytes. However the sensing studies by Coordination complex, specifically the Coordination metal complex for the detection of hazardous analytes [4] is still an under developing research area. The main challenge of this area is to control the nuclearity of the Coordination complex, high kinetic energy barrier and the solvation energy [5] etc to meet the desired motif.

Keeping these in minds, Schiff base (HL) forms with the condensation of pyridine-2-aldehyde and 2-amino-2-methyl-1-propanol provides the tridentate NNO coordination site for binding the metal ions. Coordination Chemistry of Co(II) is a subject of interest due to its versatile behaviour, different structural diversity and several non-covalent interactions in the solid state crystal structure.

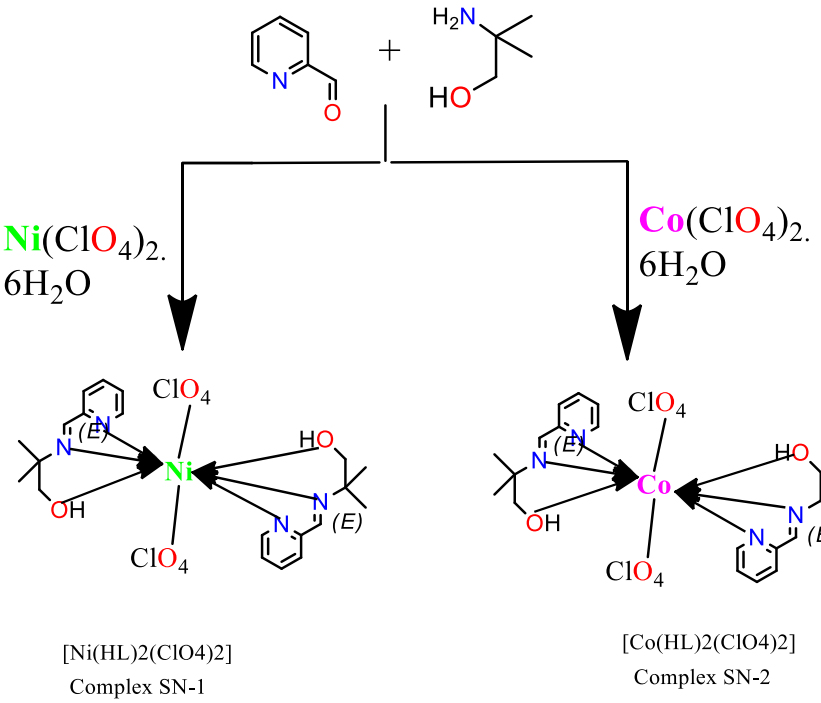
The hydrogen bonding network present in the molecule stabilizes the crystal structure [6]. The presence of intermolecular and intramolecular

hydrogen bonding in the molecular framework is extremely important in terms of physical, photochemical and sensing mechanism [7].

Hence the detection of sulfide moiety could be easily monitored with the help of hydrogen bonding in the molecular scaffold. It is noteworthy to mention that H_2S is highly toxic and flammable gas like CO, NO. The toxicity of sulfide resembles almost like cyanide in human body. High level of S^{2-} in human body can make deadly consequences to the eyes, respiratory system and nervous system. In this context, simple colorimetric probe for rapid detection of S^{2-} is of immense urge.

Herein, we report two six coordinated mononuclear complexes of Co(II) and Ni(II) among which Co(II) complex (SN-1) has been found to sense specifically the hazardous analyte S^{2-} up to nano molar range both in the solution state as well as in the gaseous phase. The easy synthetic procedure, the rapid naked eye colour change and the very low level detection for this hazardous analyte without using sophisticated instrument makes our work unique.

Present Work:



Scheme 1: Reaction scheme of Complex SN-1 and complex SN-2.

Colorimetric change upon addition of S^{2-} (aq) to SN-1 and SN-2:

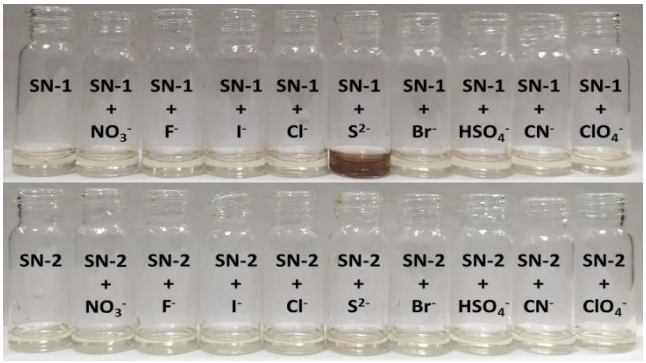


Figure 1: (up) Visual effects of SN-1 after addition of different anionic species in purely aqueous medium (down) Visual effects of SN-2 after addition of different anionic species in purely aqueous medium.

Results and discussions:

Colorimetric responses of SN-1 & SN-2 towards S^{2-} in purely aqueous medium:

The colorimetric responses of SN-1 & SN-2 (10^{-4} M, DMSO) were investigated in presence of different targeted anions. It was found that a colorimetric alteration from light yellow to blackish brown (Figure 3, up) was observed in case of SN-1 after addition of S^{2-}, whereas for other anionic contaminants, there were no such observations. In addition, there was no naked eye colorimetric transformation for SN-2 after addition of targeted analytes. Both the chemosensors remained silent after addition of same equivalent of cationic contaminants.

Spectro-photometric response of SN-1 towards S^{2-}:

In order to investigate the mechanistic pathway of host-guest interaction, we have carried out the UV-Vis titration of SN-1 (10^{-5} M, DMSO) with the targeted analyte S^{2-} (10^{-3} M, H_2O). The absorbance spectrum of SN-1 in DMSO showed a discrete peak at ~270 nm due to ligand localised π-π* transition. In addition, there was a minor contribution from intra-ligand charge transfer overlapped with metal based charge transfer due to $M_{d\pi}$-HL_{π^*}. As an artefact, the colouration of the metal complex occurred. The addition of the guest analyte (S^{2-}) changed the intramolecular electronic configuration leading to gradual increase of the MLCT peak at ~370 nm with an isosbestic point at

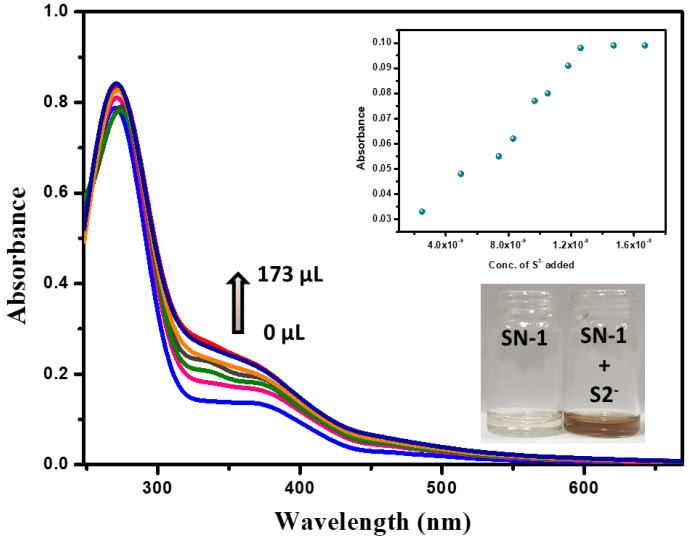


Figure 2: UV-Vis absorption spectra of SN-1 (10^{-4} M, DMSO) after addition of S^{2-} (10^{-3} M, H_2O) in purely aqueous medium; Inset: Change of absorbance at 370 nm as a function of S^{2-} added.

~290 nm. The overall change in electronic property leads to naked eye colorimetric alteration from light yellow to blackish brown. The association constant was calculated to be 11.05×10^8 M^{-1} from B-H plot

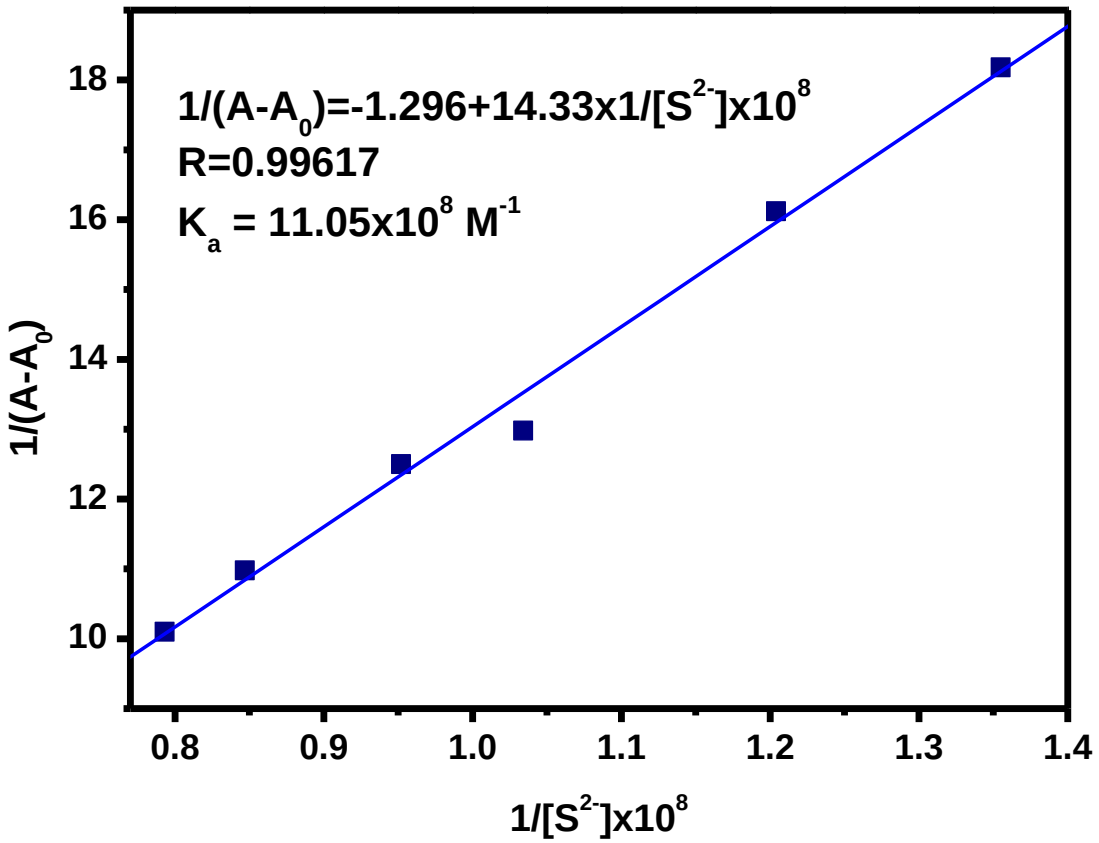


Figure 3: Benesi–Hildebrand (B-H) plot for absorbance of S^{2-} with Complex SN-1 for the association constant determination (Figure 2).

and a good linear function of absorbance vs concentration of analyte was found in the concentration range of 0.007-0.126 μM. The LOD (limit of detection) was found to be 33.5 nM (Figure 4).

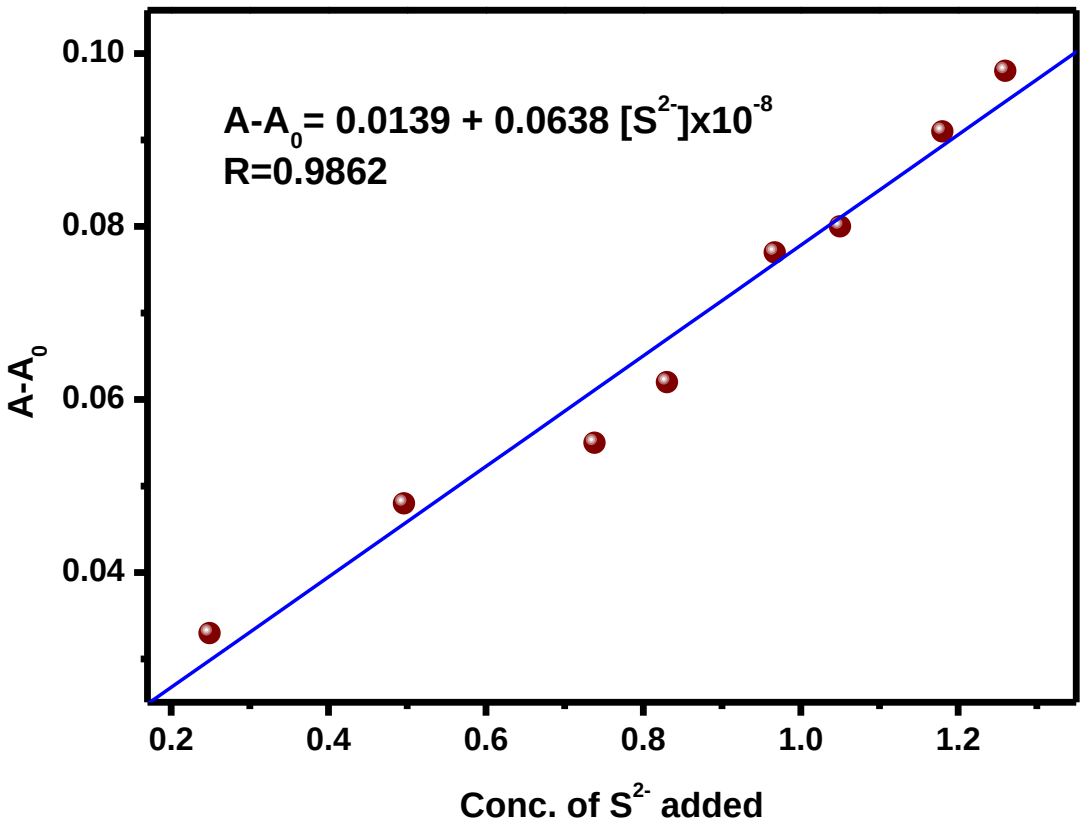


Figure 4: change of absorbance as the function of the concentration of S^{2-} for the calculation of LOD of the Complex SN-1 towards S^{2-}.

In order to evaluate the selectivity of the developed chemosensor, we have investigated the effect of other cationic as well as anionic contaminants. Figure 4, clearly indicates the selective nature of the SN-1 towards S^{2-} even in coexistence of other contaminants.

Mass spectrometry: The sensing mechanism could be explained nicely with the help of mass spectrometry. SN-1 was dissolved in DMSO solvent and the data was recorded in mass spectrometry. To have the idea about the structure of the complex, sodium sulfide taken in aqueous solution was added to SN-1 and again the mass data of the resulting solution was recorded. The molecular ion peak was found at 757.4563 which suggest that the DMSO and MeOH coordinate with the complex as shown in the scheme 3. The base peak at 240.9852

suggests the symmetrical cleavage of the molecule as shown in the scheme 3.

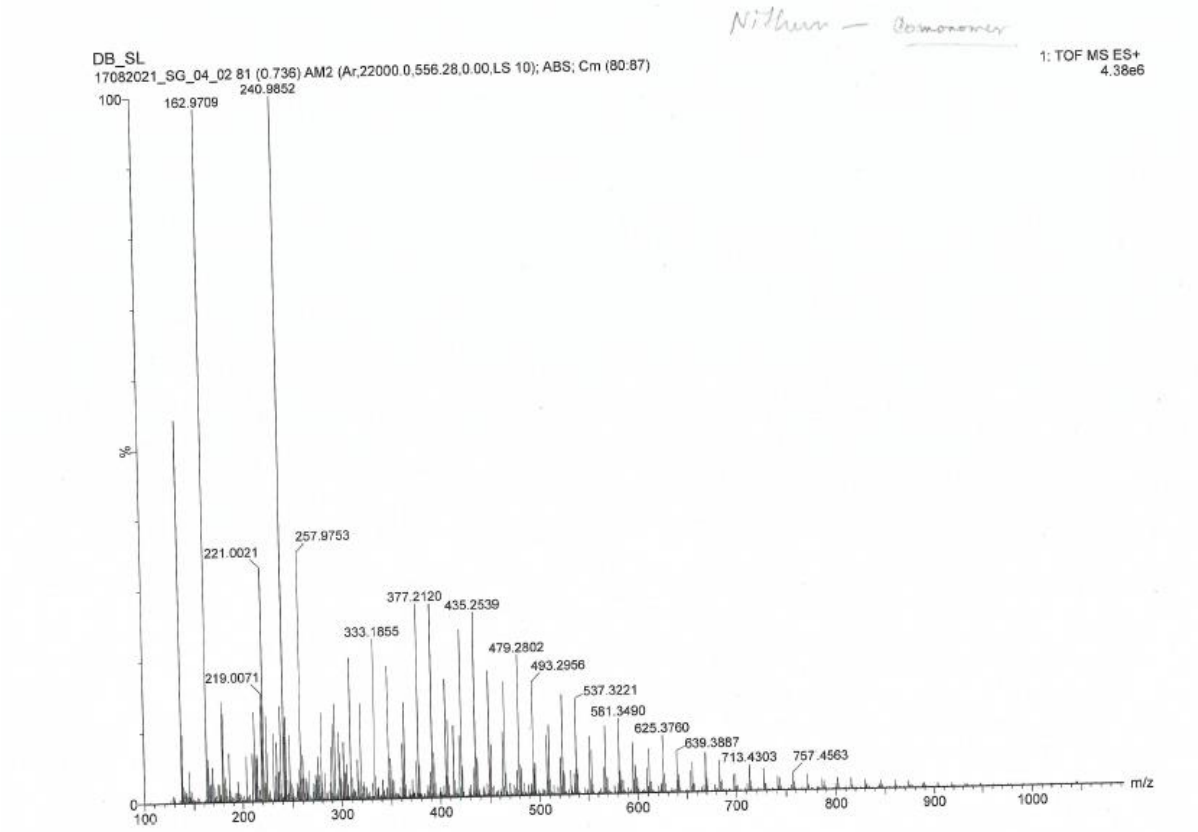
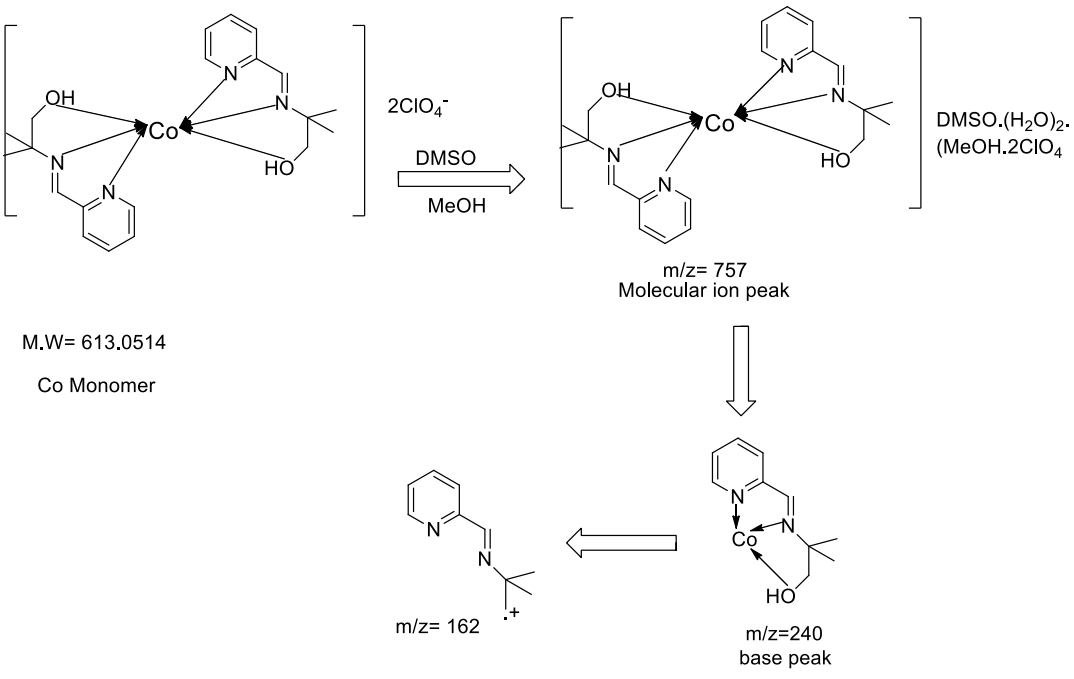


Figure 6: Mass spectrometry of the Complex SN-1 in DMSO-MeOH



Scheme 3: Probable Mass spectrometry analysis of the complex SN-1

When Sulfide was added to the DMSO solution of SN-1, the molecular ion peak at 447 and the base peak at 414 suggests the incorporation of –SH to the complex and the formation of the probable complex are shown in scheme 4.

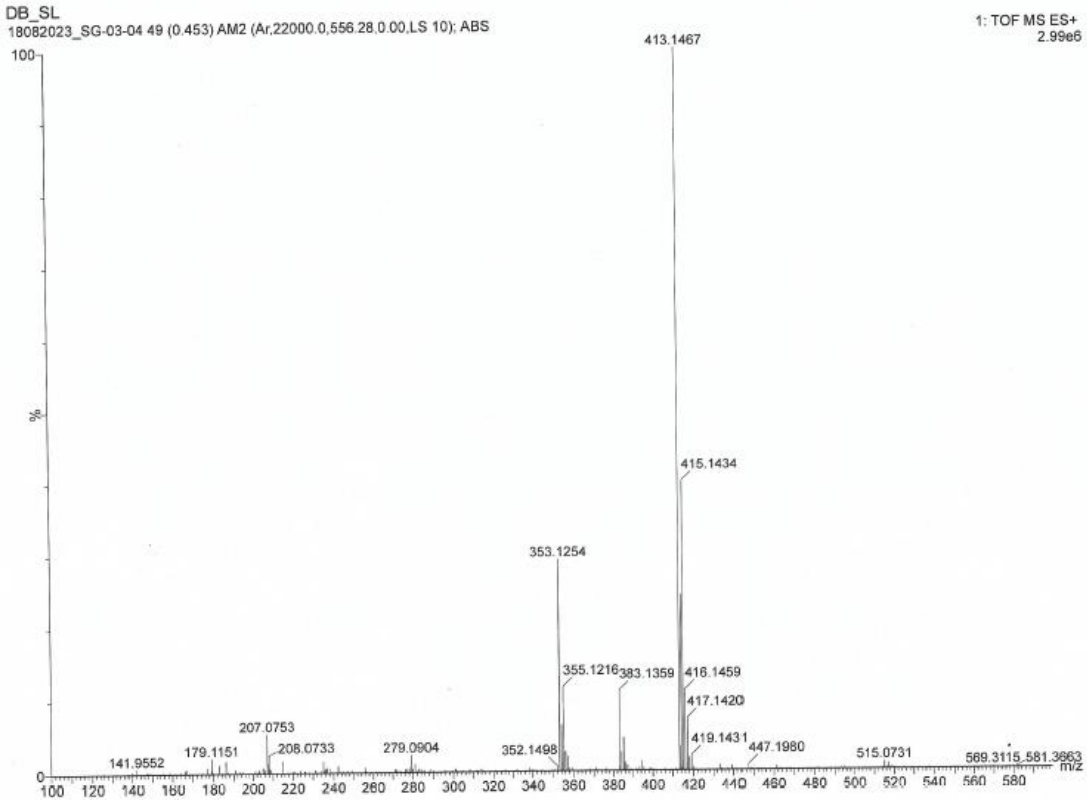
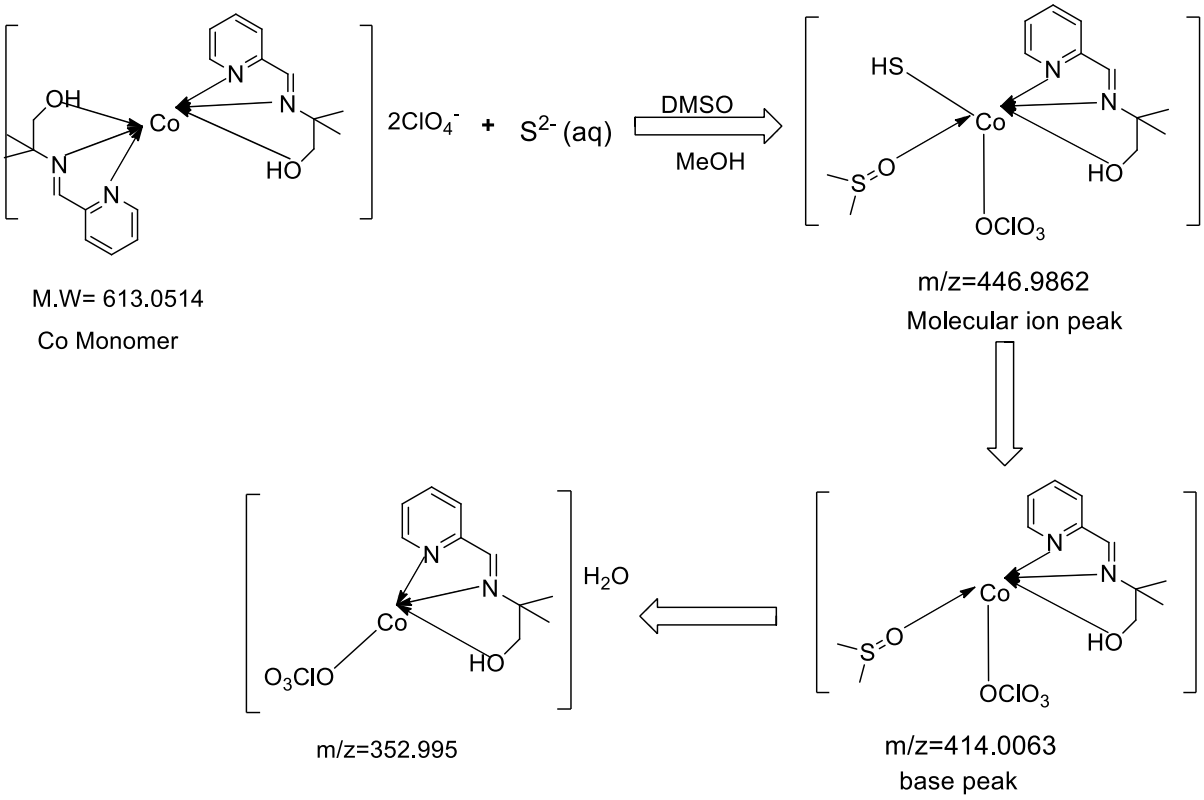


Figure 7: Mass spectrometry of the Complex SN-1 with sulfide in DMSO-MeOH



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Scheme 4: Probable Mass spectrometry analysis of the complex SN-1 with sulfide

Conclusion: Herein, we have synthesized two mononuclear metal [Co(II) & Ni (II)] complexes amongst which SN-1 has been found to recognise the hazardous analyte S^{2-} up to the nano molar range. The instant colour change in the visual range makes the chemosensor applicable for on-field detection. Judicious choice of metal centres makes SN-1 selective towards S^{2-} compared to SN-2. The proposed host-guest interactive mechanism has been experimentally as well as theoretically corroborated. Easy synthetic procedure, low level of detection of hazardous analyte and instant detection makes a new insight in the field of material science. This material could be administered for the instrumentation like "Point-of-care" device for the detection of sulfide from aqueous as well as other biological matrices.

Reference:

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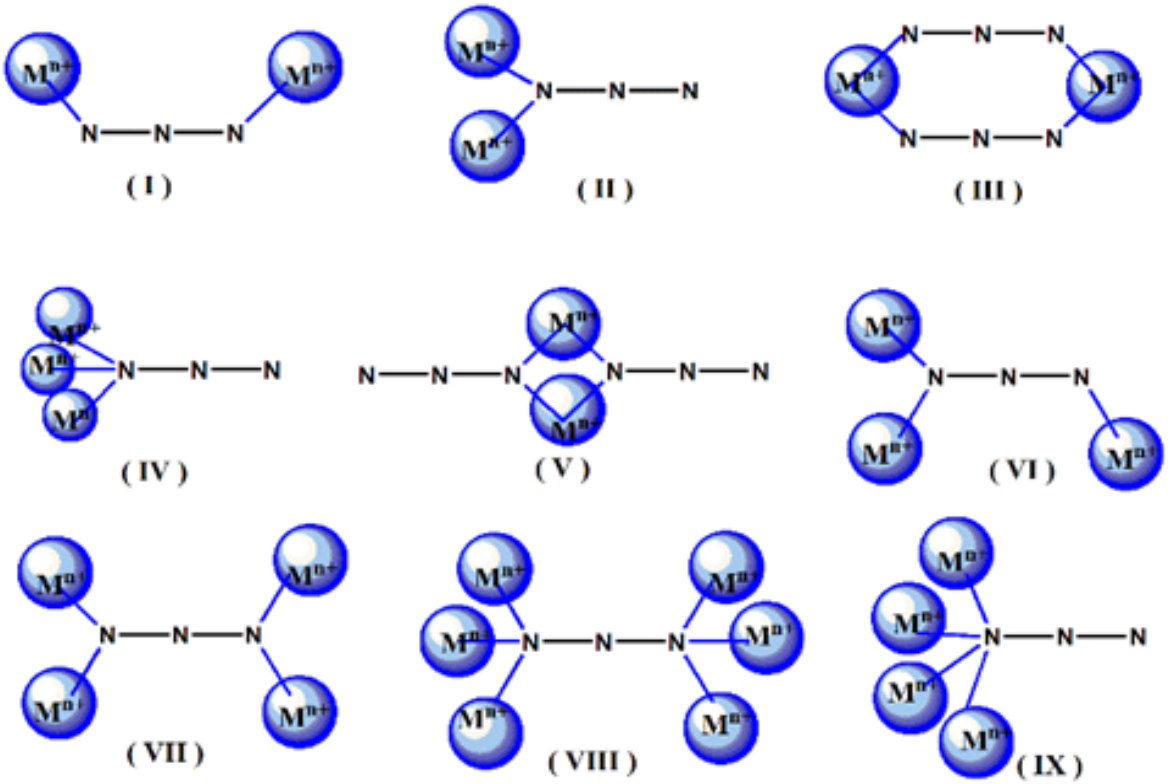
Chapter 2

Exploratory studies on azido-bridged pincer metal [Ni(II) and Mn(II)] clusters as ditopic colorimetric chemosensor for S^{2-} and Ag^{+}: Combined experimental and theoretical outcome with real field application

Introduction:

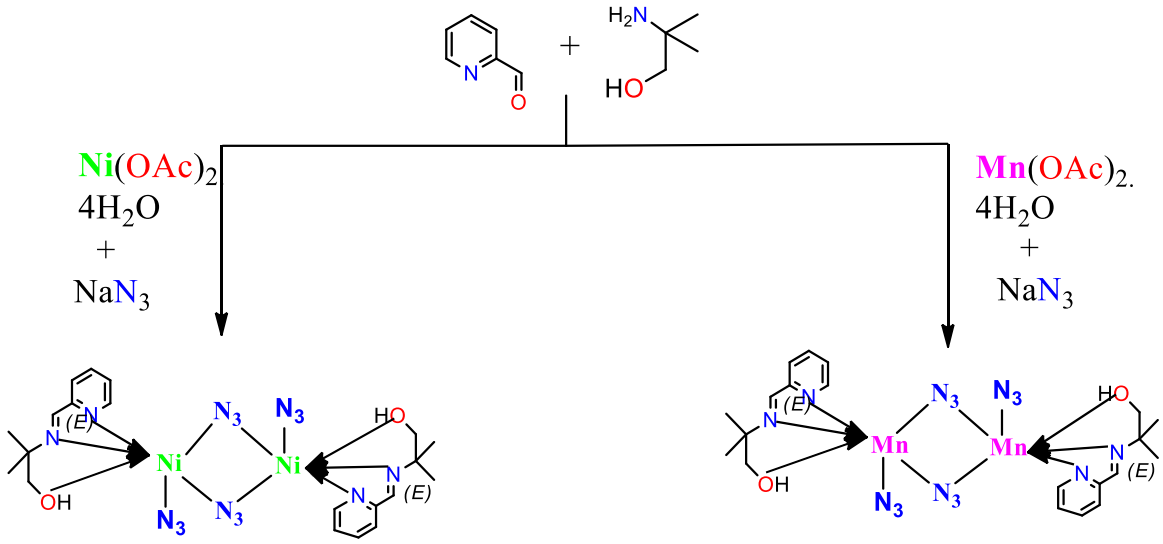
Azide plays a ubiquitous role in coordination chemistry and specifically the inorganic azide, N_3^-, represents the most widely used form to date. The coordination modes of N_3^- vary from mono-dentate to hexa-dentate (vide. Scheme 1) with the tetra- & hexa-dentate modes representing the more rare examples [1], and notably several complexes of high nuclearity and coordination polymers are reported [2,3]. Apart from the fundamental interest in the coordination chemistry of this ion with metal complexes, azido bridged complexes exhibit interesting magnetic properties as well can be used to transfer an “N” atom to a substrate [4]; thus their applications sensing probes towards external toxic analytes is an underdeveloped research area [5].



Scheme 1: Different coordination modes of azide co-ligand

In this relevance, two azido-bridged, N,N,O-donor Schiff base ligand based transition metal [(Ni(II) and Mn(II)] complexes (BS-1 & BS-2) have been synthesised for selective and sensual detection of the targeted analytes (S^{2-}, Ag^{+}).

Present work:



Complex -1 (BS-1)

$[Ni_2(HL)_2(N_3)_4]$

Complex-2 (BS-2)

$[Mn_2(HL)_2(N_3)_4]$

Result and discussions:

Colourimetric responses of BS-1 towards S^{2-} in an aqueous medium: The colourimetric response of the BS-1(10^{-5} M) in DMSO medium towards different anions was examined and it was observed that a drastic colour change from light yellow to brown was observed only for sulfide (Figure 1) whereas other anions did not have any effect.

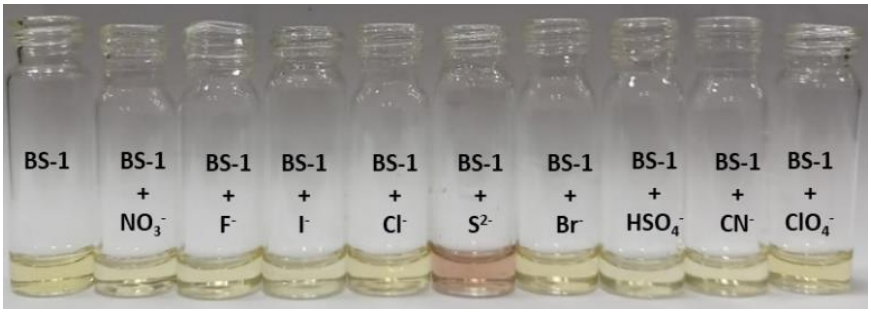


Figure 1: Visual effects of BS-1 in DMSO medium towards different anions in purely aqueous phase

In order to investigate the interaction of the BS-1 with various anions & cations, UV-Vis titration of the chemosensorwas carried out at room temperature using the salt solution of the targeted analytes. The spectrum of BS-1 in DMSO medium exhibited a discrete peak at 275 nm due to the ligand-localised π-π* transition. The π-π* transition corresponds to the transition in the aromatic pyridine moiety [6]. In addition to this, a minor contribution from low-energy transition is assigned due to ICT (Intra-ligand change transfer) overlapped with a MLCT ($M_{d\pi}$-HL_{π^*}) leading to the overall colouration of the metal complex [7]. The addition of S^{2-} to the chemosensor solution leads to the change of electronic propertyvia reduction of N_3 to NH_2 of BS-1. The peak at 275 nm was reduced with the concomitant increment of the MLCT peak at 315 nm (Figure 2) with a well-anchored isosbesticpoint at 290 nm. Thisleads to a vivid naked eye colour change from light yellow to brown.

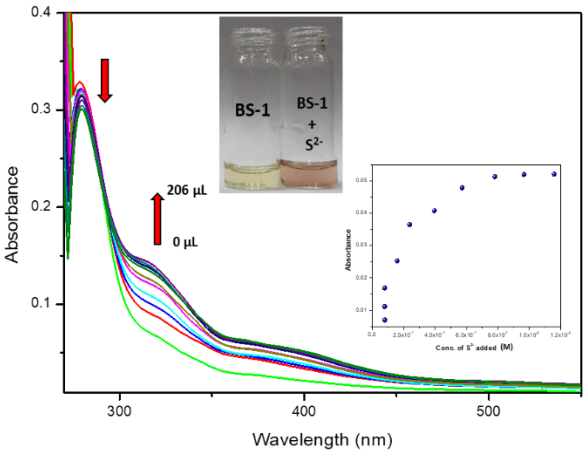


Figure 2: UV-Vis absorbance change of BS-1(10^{-5} M) in DMSO medium with the gradual addition of S^{2-}(10^{-4} M) in an aqueous medium at room temperature. Inset: absorbance at 315 nm as a function of the equivalence of S^{2-} ions added

Spectrophotometric properties of the chemoreceptor BS-2 with Ag^{+}:

Colorimetric responses of BS-2 towards Ag^+ in the semi-aqueous medium: The colourimetric responses of BS-2 (10^{-4} M, DMSO) with different cationic solutions in MeCN:H_2O (9:1; v/v) medium was investigated. The colour of the sensor solution was changed (from greyish-yellow to decolouration) drastically (Figure 3) upon addition of Ag^+ whereas other cationic contaminants like Cu^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+} etc. remained silent upon interaction with the sensor molecule BS-2.

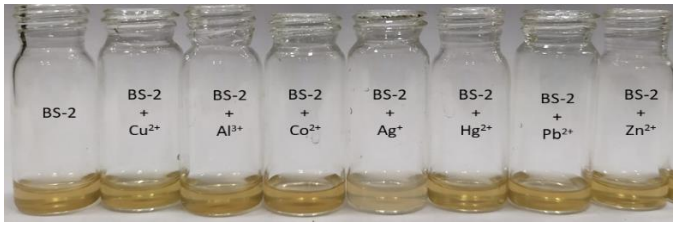


Figure 3: Visual effects of BS-2(10^{-4} M, DMSO) towards different cations in organo-aqueous (9:1; v/v) phase

UV-Vis spectra of BS-2 (10^{-4} M) in DMSO was performed which showed intense band centred at 270 nm. This low-energy band was assigned as π-π* transition of the aromatic moiety of the ligand HL. Interestingly, the colour of the BS-2 was decoloured from greyish yellow to faint yellow (Figure 3) upon interaction with the targeted analyte, Ag^+ ion. The gradual diminish in the absorption peak position infers change in the electronic property within the molecular scaffold upon gradual addition of Ag^+. Herein, the electron rich azide centres provide an excellent binding sites for Ag^+ ion leading to the decolourisation of the chemosensor BS-2. This affirmed the interaction between host (herein BS-2) and guest analyte (herein Ag^+).

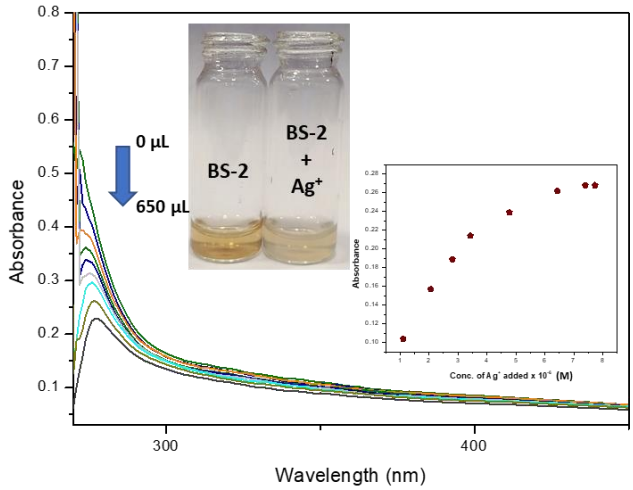


Figure 4: UV-Vis absorbance change of BS-2 (10^{-4} M) in DMSO medium with the gradual addition of Ag^+ (10^{-4} M) in MeCN:H_2O (9:1; *v/v*) medium at room temperature. Inset: absorbance at 270 nm as a function of the equivalence of Ag^+ ions added.

Real Field Application:

To investigate the practical implementation of the chemosensor BS-1, test paper strips were prepared by immersing paper strips (3 x 1 cm^2) into a DMSO solution of BS-1(10^{-3} mol/L) followed by air drying for overnight [8]. The test strips were utilised for detection of S^{2-} in solution phase as well as in gaseous phase. A distinct colour change was observed from light yellow to brown (Figure 5) when S^{2-}/H_2S came into vicinity of the paper strips with the help of "Dip-stick" approach. Thus detection of this lethal toxic element (S^{2-}/H_2S) can be done on field instantly using this test strip without the assistance of any

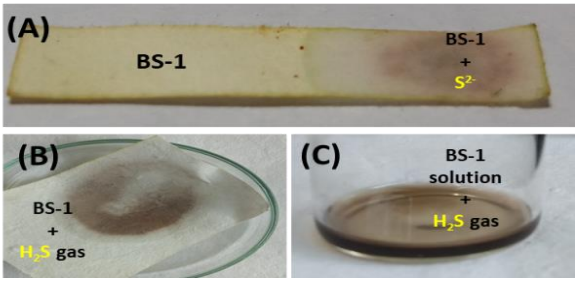


Figure 5: A) Test strip coated with BS-1 sensor upon interaction with S^{2-} (B) Test strip of BS-1 after interaction with H_2S gas (C) Solution of BS-1 after interaction with H_2S gas

costly instrumentation. A comparative literature survey of BS-1 with other S^{2-} & Ag^{+} sensors was also performed which expressed the superiority of our developed system.

Conclusion: In brief, we report the synthesis and characterisation of two dinuclear complexes BS-1 and BS-2 and their use as molecular sensors towards hazardous entities. Proper tuning of the molecular probe makes the system BS-1 highly selective for dual sensing of S^{2-} and Ag^{+} while BS-2 for Ag^{+} only.

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Chapter 3

3d-4f single molecular magnet with considerable anisotropy of magnetisation in Fe_4-Ln_2 (Ln = Dy(III), Tb(III) and Er(III)) complexes

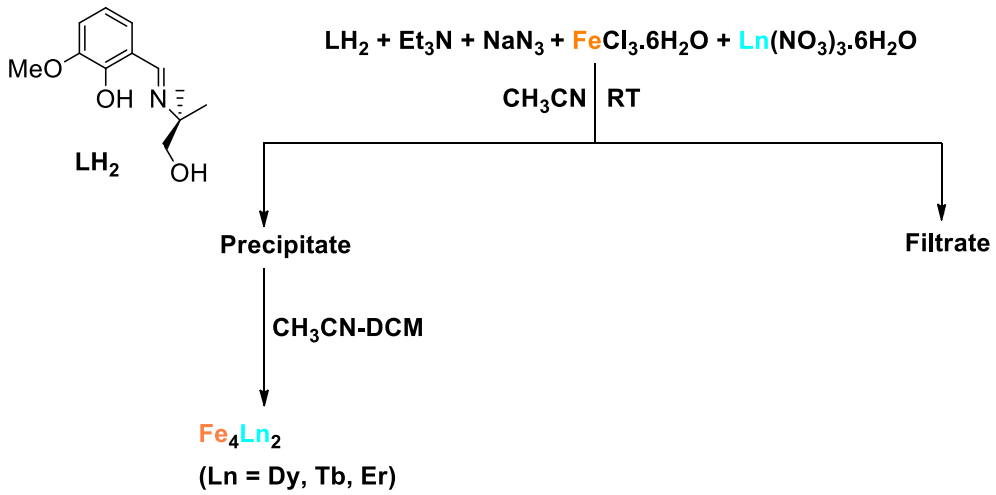
Introduction:

Metal Organic Framework is one of the most emerging fields in chemistry [1] due to its potential application in the field of gas storage, catalysis, drug delivery, adsorption, energy storage, super-capacitor, conducting material, sensing and magnetism. Single molecular Magnet (SMM) is one of the prominent research areas for physicists and chemists due to its slow magnetic relaxation below the characteristic blocking temperature (T_B) which includes vast application of magnetic material as high density memory storage device, quantum computing and molecular spintronics [2]. High spin values (S) and large negative axial magnetic anisotropy (D) is the fundamental requirement to increase the anisotropic energy barrier (U_{eff}) to the reversal of molecular magnetization [3]. MOFs composed of first row transition metal (3d metals) with maximum number of unpaired electrons are the excellent candidate to be SMM as far as the spin state is considered. However the magnetic anisotropy of the 3d metals is not so high. Introduction of trivalent rare earth metal cations (4f) produces high magnetic anisotropy [4] to the magnetic moment although weak magnetic interactions are sometimes observed due to shielding effect. A combination of two different spin carriers within the same molecule, particularly the heterometalic 3d-4f is the current strategy for the development of SMMs with diverse magnetic behaviour. Several linkers such as oxo, hydroxyl, azide, thiocyanate, carboxylate [4] may form a bridge in between metal centres and may exchange information through the linker. Hence our main interest lies on the study of the new

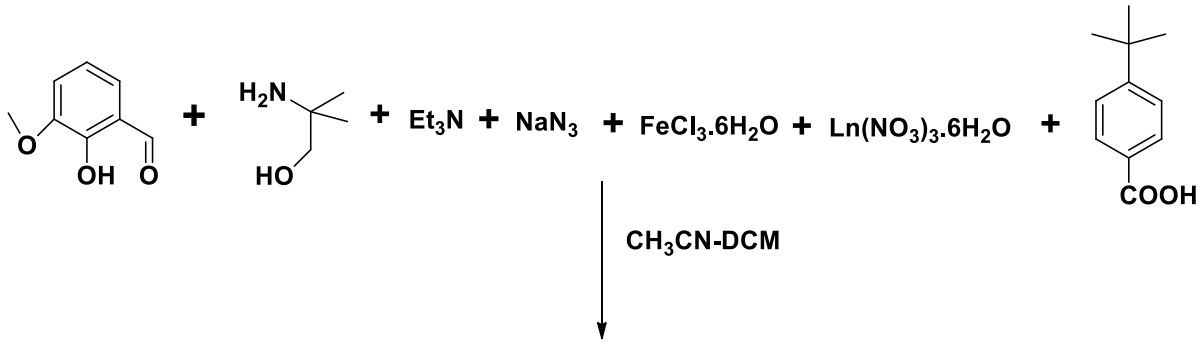
set of magnetic material comprised of 3d-4f system. We use Fe-template as a precursor for the synthesis of MOFs. Dy(III), Tb(III) and Er(III) are the excellent candidate for our synthetic strategy.

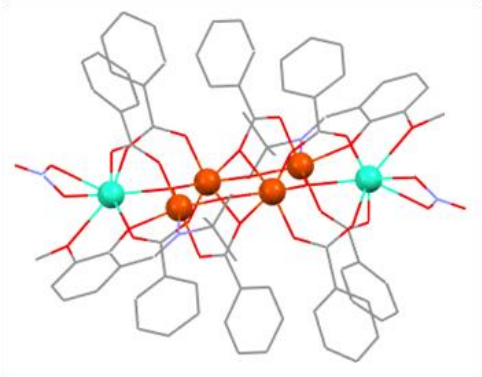
Herein, we have synthesized three new Fe_4-Ln_2 compounds (complex-1, complex-2 and complex-3) and investigated their magnetic properties. It has been found that the complex-1 and complex-2 shows Ferromagnetic behaviour however the overall interaction was found to be anti-ferromagnetic at room temperature and the $\chi_M T$ value 25.041 cm^3mol^{-1} K and 22.217 cm^3mol^{-1} K at 25 K whereas complex-3 shows only anti-ferromagnetic interactions. These molecular-based magnetic materials could give rise to original solution in data-storage application [6].

Present Work:



Scheme:





Hydrogen atoms are tert-utyl groups are ommitted for the clarity

$[Fe_4Ln_2L_2(But\text{-}PhCO_2)_8(\mu_3\text{-}O)_2(NO_3)_2]$

Where Ln = Dy, Er and Tb

Result and discussions:

The magnetic susceptibility data for a polycrystalline dried sample of complex-1, complex-2 and complex-3 were collected in the temperature range 2–300 K in an applied magnetic field of 1 T to investigate the nature and magnitude of the exchange interaction propagated by different bridging groups. A plot of $\chi_M T$ vs. T (temperature) is displayed (in Figure 1) and Plots of magnetic susceptibility $\chi_M T$ against temperature for complex-1, complex-2 and complex-3 in an external magnetic field of 1000 Oe are shown. The product of magnetic susceptibility and the temperature is a quantity which is proportional to the square of the effective magnetic moment of a molecule and is given by $\mu_{eff} = 2.82787\sqrt{\chi_M T}$. From the approximation, the curie constant for 3d ions having quenched orbital momentum is given by:

$C = \frac{N_A g^2 \mu_B^2}{3K_B} S(S+1)$ and that for 4f ion is $C = \frac{N_A g^2 \mu_B^2}{3K_B} J(J+1)$,where N_A is Avogadro number, μ_B is the Bohr magneton, K_B is the Boltzmann constant g is the Lande' g factor which is given by $g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$. Hence in the simplified form we can write $\chi_M T = \frac{\mu_{eff}^2}{3K_B} N_A$. For high spin free Fe(III) ion, magnetic moment value is 5.916 BM and for free Dy(III) ion magnetic moment value is 10.64 BM. At room temperature the observed $\chi_M T$ values are 28.649 cm^3Kmol^{-1}, 25.735cm^3Kmol^{-1} and 23.156 cm^3Kmol^{-1} for complex-1, complex-2 and complex-3 respectively. For non-interacting Dy(III) ions ($^6H_{15/2}$, S=5/2 ,L=5, J=15/2, g=4/3, $\chi_M T$=14.17 $cm^3mol^{-1}K$) and Fe(III) ions ($^6H_{5/2}$, S=5/2, L=0, J=5/2, g=2, $\chi_M T$=4.336 $cm^3mol^{-1}K$), the $\chi_M T$ value for no coupling situation in complex-1 is 26.255 cm^3Kmol^{-1} which is slightly smaller than the experimental value of 28.649 cm^3Kmol^{-1}. The similar behaviour is observed for complex-3. For non-interacting Er(III) ions ($^4I_{15/2}$, S=3/2, L=6, J=15/2, g=6/5, $\chi_M T$=11.5 $cm^3mol^{-1}K$) and Fe(III) ions, the theoretical value for no coupling situation is 21.230 cm^3mol^{-1} is also smaller than the experimental value 23.16 cm^3Kmol^{-1}. However in complex-2 for non-interacting Tb(III) ions ($^7H_4$, S=3, L=3, J=6, g=3/2, $\chi_M T$=11.82 $cm^3mol^{-1}K$) and Fe(III) ions, the observed $\chi_M T$ value for no coupling situation (29.502 $cm^3mol^{-1}K$) is slightly higher than the experimental value 25.14 $cm^3mol^{-1}K$. In Complex-1, $\chi_M T$ value decreases monotonically with decreasing temperature to reach a value of $\chi_M T$ = 25.041 cm^3mol^{-1} K at 25 K which indicates that there might be anti-ferromagnetic interactions in the complex between Dy(III) and Fe(III) centres; below 25 K. Also, there is a sharp raise reaching a value of $\chi_M T$ = 29.735 cm^3mol^{-1} K at 2 K which indicates the presence of an ferromagnetic exchange coupling between the Fe and Dy centres in complex-1, however the overall interaction of the complex-1 is anti-ferromagnetic as suggested from the $\chi_M T$ vs T plot. The effective magnetic moment at room temperature of complex-1 (15.13 BM) decreases to 14.15 BM at 25K. This decease attribute the depopulation

of the stark levels and the magnetic anisotropy [**7**] of the local Dy(III) ions. The similar behaviour is observed in complex-2. In complex-2, $\chi_M T$ value at room temperature also decreases monotonically with decreasing temperature to reach a value of 22.217 cm^3mol^{-1} K at 25 K that there might be anti-ferromagnetic interactions in the complex between Dy(III) and Tb(III) centres; below 25 K there is a sharp raise reaching a value of 28.257 $cm^3mol^{-1}K$ at 2 K. This magnetic behaviour indicates the presence of a ferromagnetic exchange coupling between the Fe and Tb centres; however the overall interaction is antiferromagnetic in nature as suggested from the $\chi_M T$ vs T plot in complex-2. However in complex-3, $\chi_M T$ value at room temperature decreases monotonically with decreasing temperature to reach a value of 17.371 $cm^3mol^{-1}K$ at 30 K; below 30 K there is a sharp drop reaching a value 10.235 cm^3mol^{-1} K at 2 K.

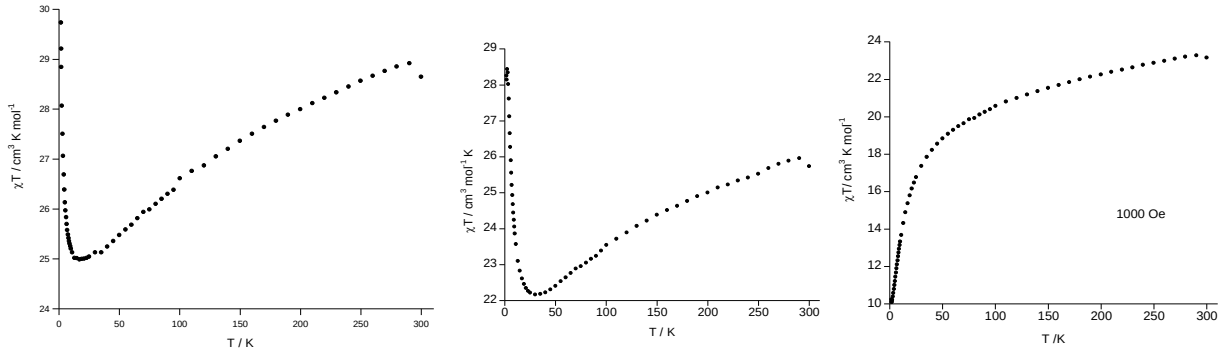


Figure 1: $\chi_M T$ vs T plot for complex-1 (left), complex-2 (middle), and complex-3 (right).

This magnetic behaviour clearly indicates the presence of overall anti-ferromagnetic exchange coupling between the Fe and Er centres in complex-3. We have done magnetization measurements at different fields but three particular temperatures (2K, 3K and 5K) for each complex to see whether magnetic anisotropy is present. Although all these complexes are iso-structural, the difference in the magnetic behaviour might be probably explained in terms of electron cloud

distribution of the lanthanide ions. The electron cloud distribution in the Dy(III) and Tb(III) are oblate however the electron cloud density for the Er(III) is prolate [8] . It is the probable reason for the difference in the magnetic behaviour in complex-3 in compare with the complex-1 and complex-2.

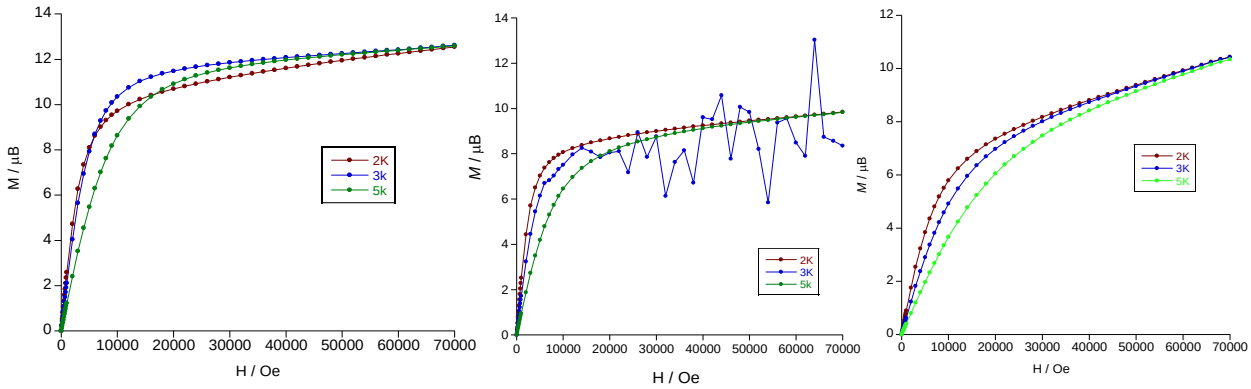


Figure 2: Magnetization curves for complex-1 (left), complex-2 (middle), and complex-3 (right).

Indeed in all the complexes the magnetisation value increases rapidly at low field and do not superimpose on each other which indicates an isotropic system with well-defined ground states. However in the higher field the magnetization curve is linear at 2K, 3K and 5K in complex-1 and complex-2 (Figure 2) which clearly reflects the significant anisotropy with low lying excited states. However the magnetization curves are not getting saturated in complex-3, which suggest that the overall interactions are anti-ferromagnetic and ground states are not well separated with the excited states. Variable temperature ac measurements were performed at 1.8-7 K for complex-1, complex-2 and complex-3 under a zero dc field oscillating at 1-1500

Hz in order to study their response to dynamic magnetic fields.

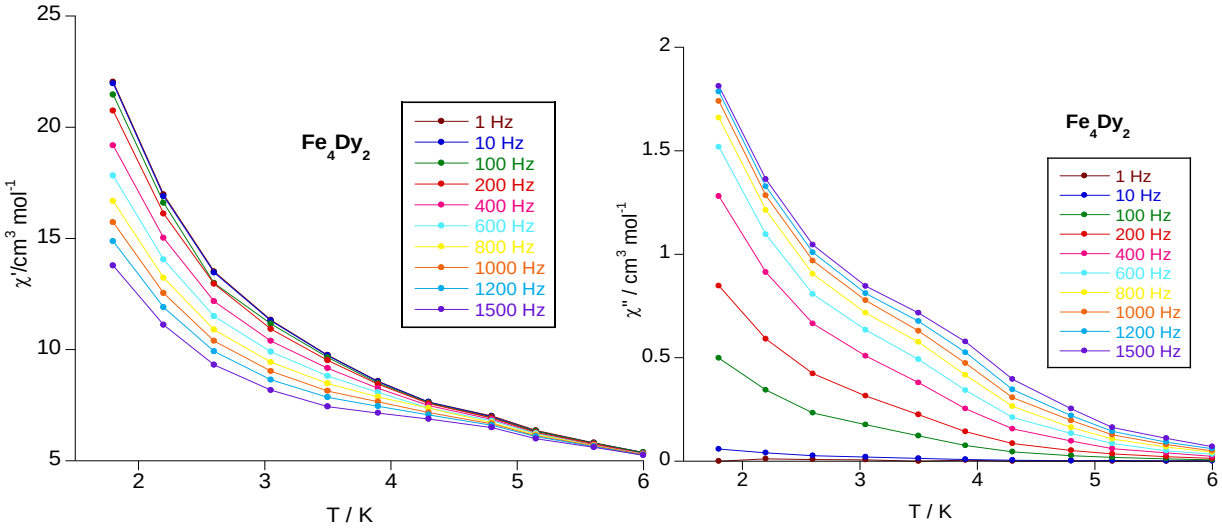


Figure 3: In-phase and out-of-phase ac susceptibility measurements of complex-1 in the range of 1.8- 6 K and 1-1500 Hz ranges.

complex-1 shows in-phase (Figure 3, left) and out-of-phase (Figure 3, right) signal, which suggests this complex is SMMs. Ac signal of those complexes does not show any peaks at lower frequency but at higher frequency it is developing one shoulder in the range of 2.5-4.5 K, which suggest significant amount of quantum tunnelling effect even at very low temperature.

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Chapter 4

An unprecedented penta coordinated end on azido Zn complex derived from N,N,O-donor clickable ligand with their application in sensing hazardous analytes S^{2-} and Ag^{+}

Introduction:

Metal organic frameworks (MOFs) are counterpart of many porous entity and pertinent material for future needs and in almost every sphere of life [1]. MOFs are a unique class of crystalline solids comprised of metal cations (or cluster) & organic ligands have potential applications as clean energy storage, sensing, high capacity adsorbents, luminescence, proton conduction, drug delivery, catalysis, magnetism & sensing [2]. Mononuclear terminal azido complex are very few in the literature.

Herein, two novel mononuclear Zn complexes i.e.[Zn(HL)(N_3)(OAc)] (complex-1) and [Zn(HL)$_2$(ClO_4)$_2$](complex-2) have been synthesised using a tridentate clickable Schiff base ligand, HL (2-methyl-2-((pyridin-2-ylmethyl)amino)propan-1-ol), and the polyatomic mono anion N_3^- and ClO_4^- for complex 1 and 2 respectively.

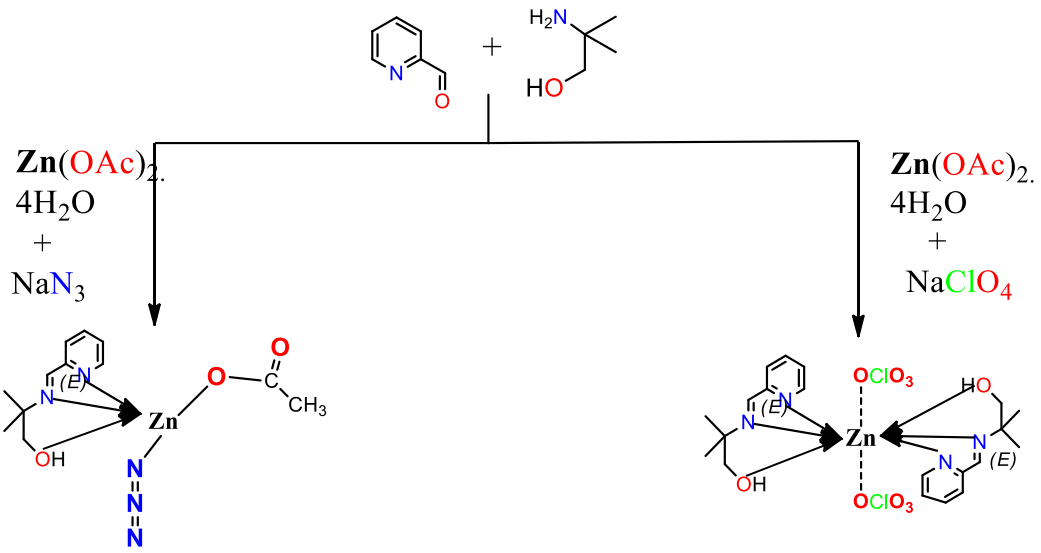
H_2S is a highly toxic and flammable gas and like carbon monoxide and nitric oxide. In terms of toxicity, its impact is comparable to that of cyanide intoxication in the human body [3]. The limit of H_2S in human blood is in the range of 10-100 µM and the central nervous system is in the range of 50-160 µM. A higher level of H_2S imposes harmful effects such as cytotoxicity and irritation to the skin and mucosa of the living bodies [4].

Silver (Ag^+) is a toxic cationic contaminant and displays fundamental role concerning human health and the environment. However, improper

disposing of this metal may damage aquatic lives and may accumulate in the human body through the food chain.

The metal cluster Complex-1 showed high selectivity towards S^{2-} and Ag^{+} with a naked eye colour change of light yellow to brown and light yellow to colourless respectively whereas complex-2 does not show any sensing activity due to absence of azide ion.

Present work:



Result and discussions:

Infra-Red spectroscopy: The sharp band at 2066 cm^{-1} corresponds to the azide ion. The C-H bands are at 3088 cm^{-1} and 2973 cm^{-1}, broad

band at 2816 cm^{-1} corresponds to -OH of the protonated Schiff base ligand. Band at 1752 cm^{-1} corresponds to the C-N bond of the Schiff base, another band at 1603 cm^{-1} corresponds to the C-O of acetate ion which is directly attached with Zn in complex-1.

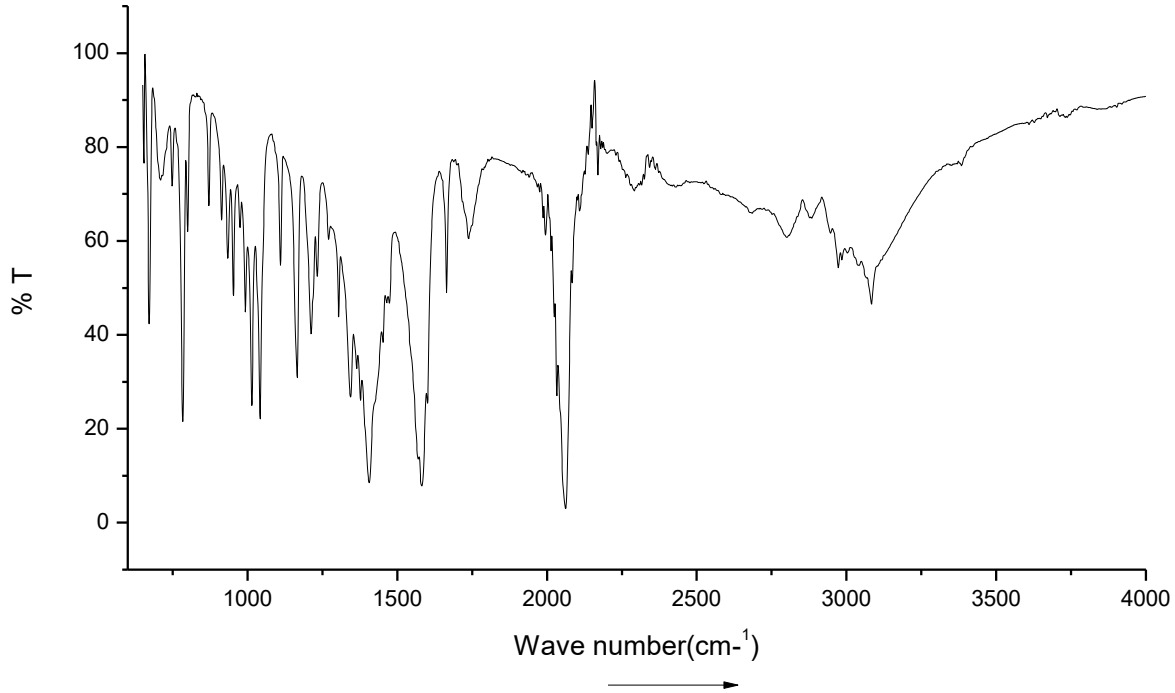


Figure 1: IR spectra of the complex-1.

The broad band at 3373 cm^{-1} corresponds to the protonated -OH of the Schiff base in complex-2. Medium band in the region 2988-2909 cm^{-1} correspond to the C-H stretching frequency. The band in the region 1074-1191 cm^{-1} corresponds to the ClO_4^-. Strong band at 1660 cm^{-1} corresponds to the C-N of the Schiff base.

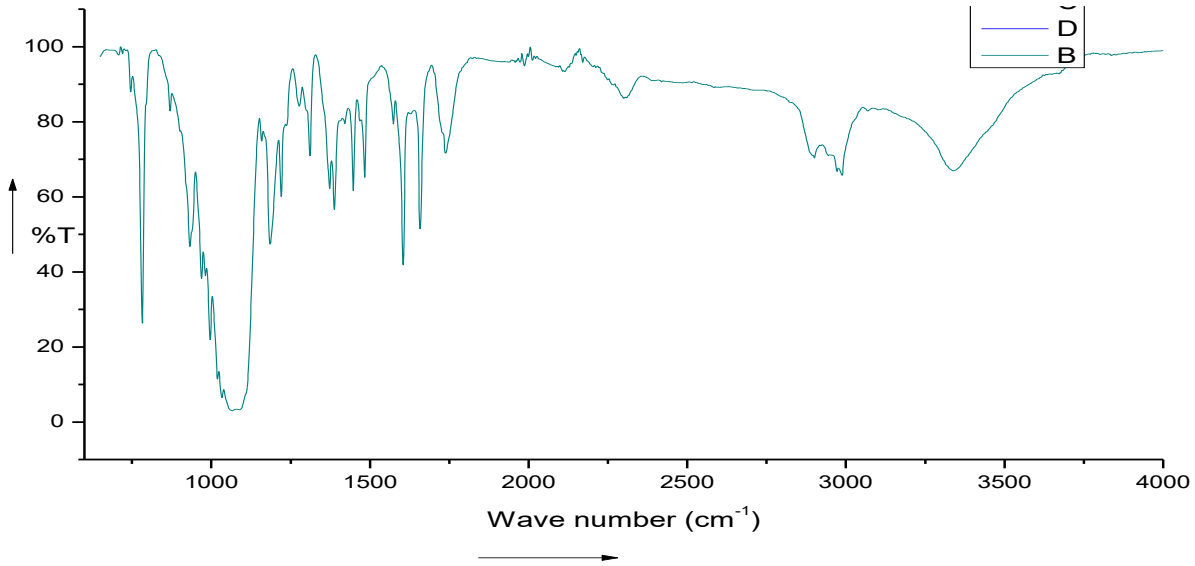


Figure 2: IR spectra of the complex-2.

Electronic Spectroscopy: The spectrum of complex-1 in CH_3CN medium exhibited a discrete peak at 263 nm due to the ligand-localised π-π* transition. The π-π* transition corresponds to the transition in the aromatic pyridine moiety [5]. In addition to this, a minor contribution from low-energy transition is assigned at 232 nm due to ICT (Intra-ligand change transfer) overlapped with a MLCT ($M_{d\pi}$-HL_{π^*}) leading to the overall colouration of the metal complex. Whereas complex-2 π-π* transition shifted to lower energy at 287 nm compare to 263 nm of the complex-1. However the MLCT transition of the complex-2 is at 234 nm which is almost similar to complex-1.

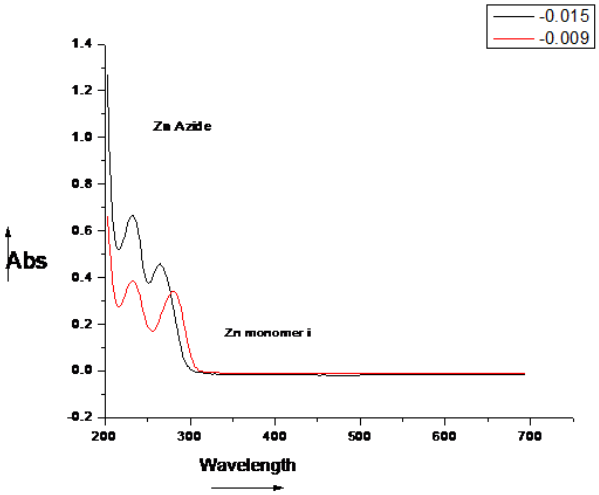


Figure 3: UV-Visible spectra of the complex-1 and complex-2 in MeOH.

Mass spectrometry:

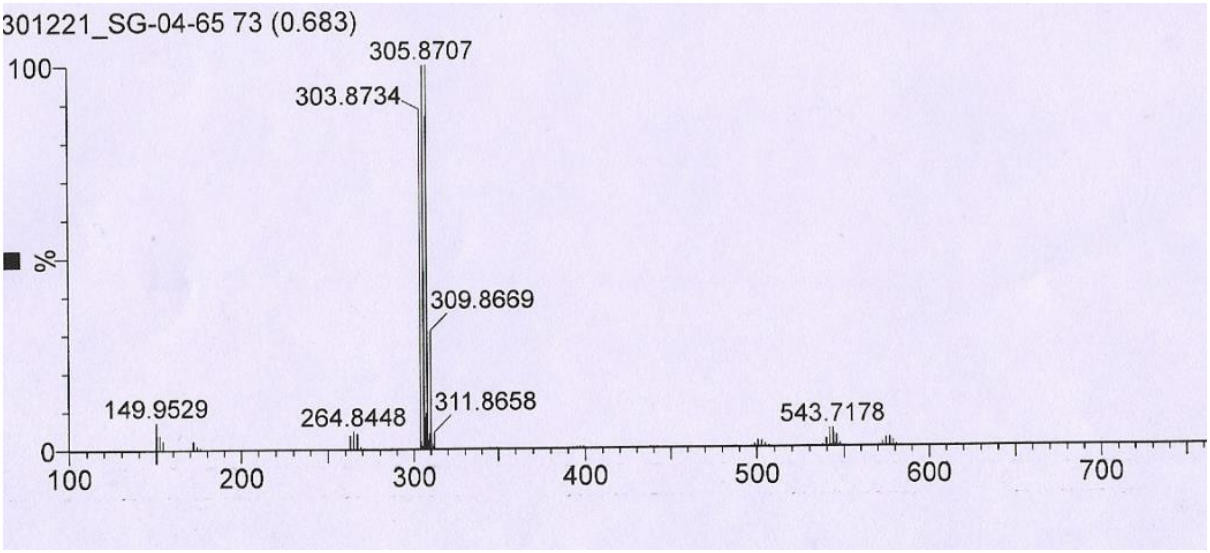
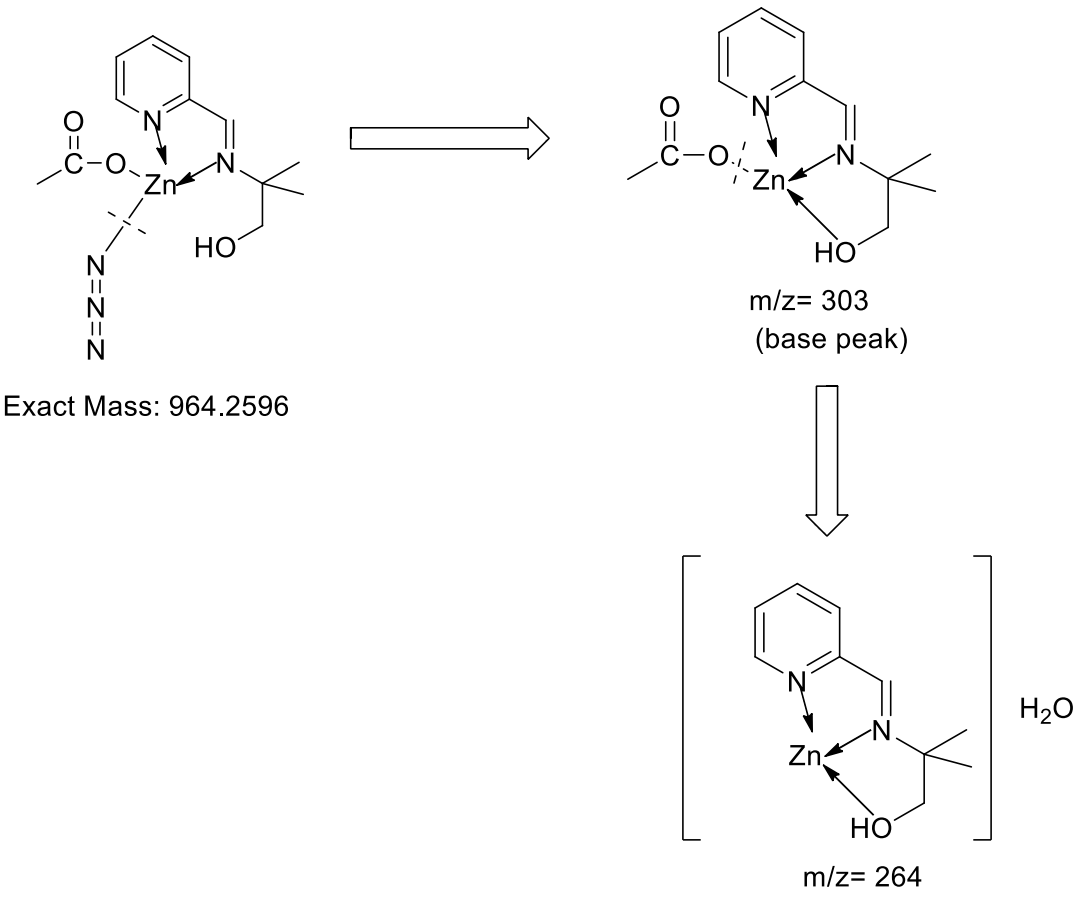


Figure 4: Mass spectrometry of the complex-1**.**



Scheme 1: Probable analysis of the Mass- spectrometry.

NMR Spectroscopy: Due to the higher solubility in D_2O, complex-1 was dissolved in D_2O and the NMR spectra were recorded. The characteristics NMR peaks of the complex-1 are: sharp singlet at 8.73 ppm for imino hydrogen, broad singlet at 8.56 ppm for the -OH of the amino alcohol which is coming from the Schiff base, aromatic protons in the range between 7.69-8.14 ppm, a sharp singlet for the two methylene protons at 3.5 ppm, sharp singlet for the 3 hydrogen atoms of the acetate group attached with the Zn at 1.79 ppm and another sharp singlet for 6 methyl protons at 1.32 ppm.

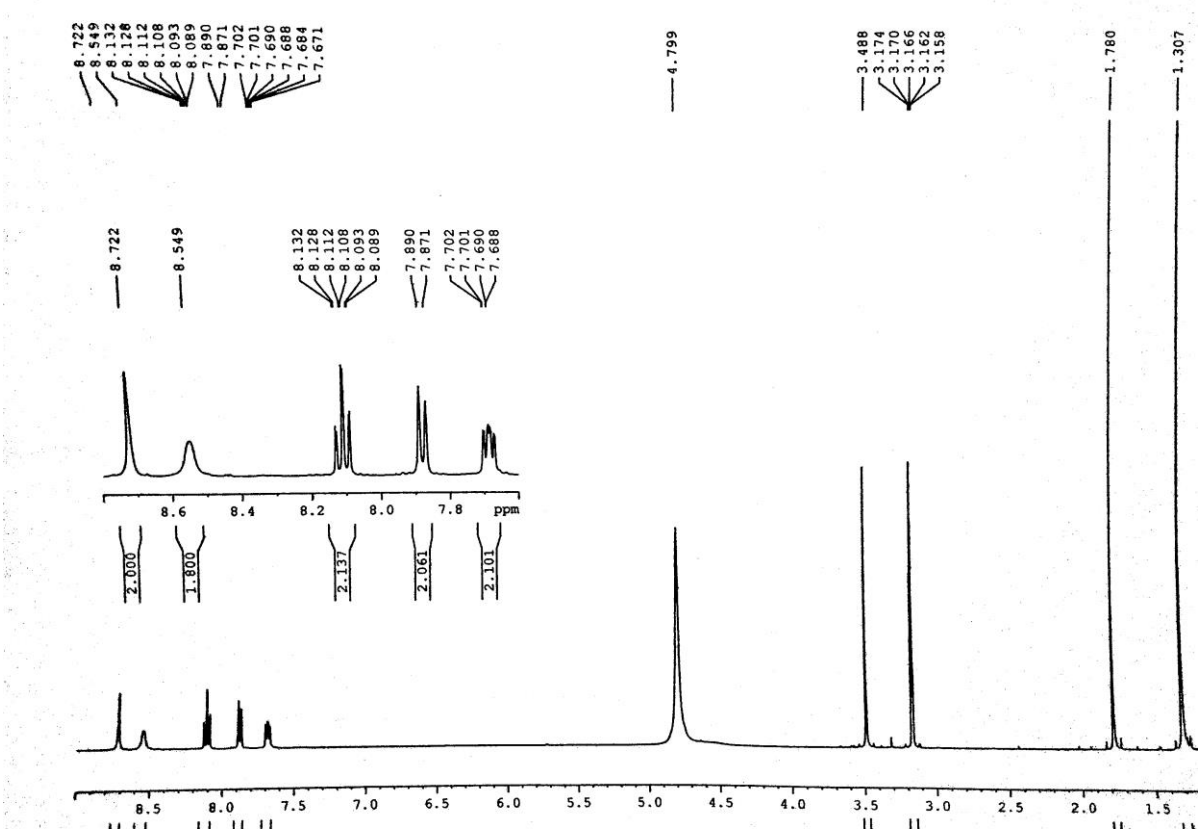


Figure 4: NMR spectra of the complex-1 in D_2O.

NMR titration of Complex-1 towards S^{2-} in D_2O medium: Mononuclear bent azido complex was dissolved in NMR solvent D_2O and D_2O solution of F^- , Cl^-, Br^-, I^- , SCN^-, SO_4^{2-}, HCO_3^-, $[Fe(CN)_6]^{4-}$,NO_3^-, and S^{2-} were added and the ^{1}H-NMR spectra was recorded. It was observed that there was no characteristic change in the NMR spectra except S^{2-}. Hence the NMR spectra of complex-1 were monitored with the gradual addition of S^{2-} in order to investigate the sensing mechanism. In the bottom of the stack plot, it is the NMR

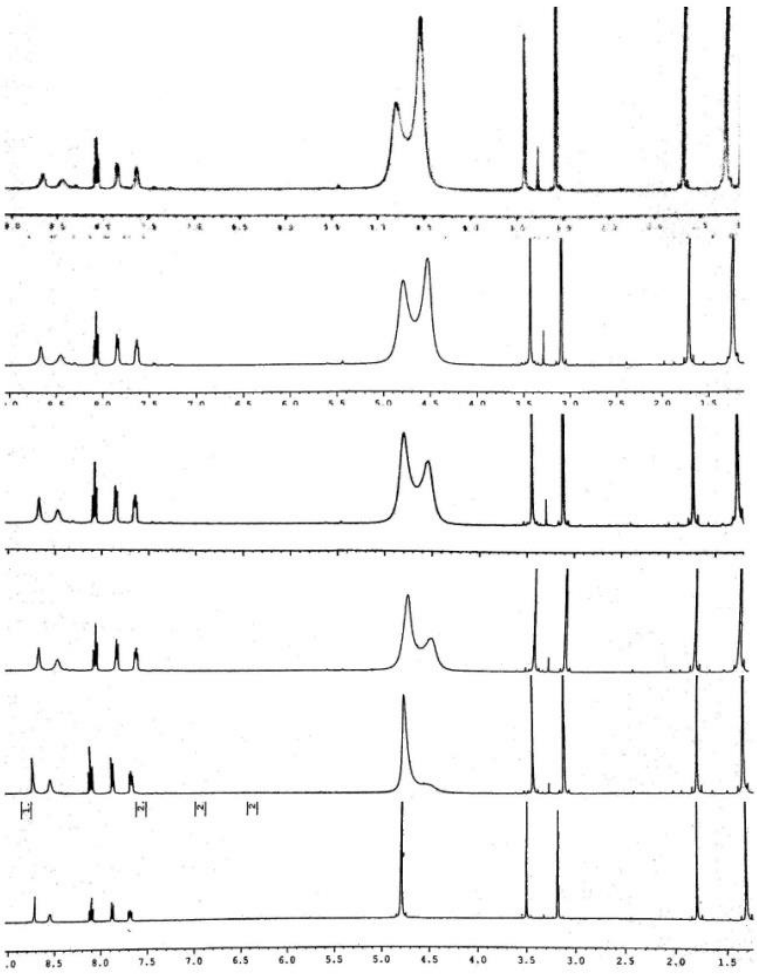


Figure 5: NMR titration of the complex-1 up on gradual addition of sulfide up to 150 µl.

spectra of the complex-1. When 10 µl S^{2-} was added there was practically a very little change. However when the concentration of Sulfide was gradually increased from 20µl to 150 µl, noticeable changes was observed. When the concentration of Sulfide was 20 µl, a broad peak at 4.6 ppm was observed. On further addition of Sulfide to the chemosensor complex-1, the intensity of the peak increases due to reduction of azide to amine which is evident from IR spectroscopy as well. The broad non-integrable peak at 4.6 ppm is a characteristic peak for aliphatic amines. The complex-1 acts as an effective Sulfide sensor which is evident from the NMR titration due to reduction of azide by Sulfide.

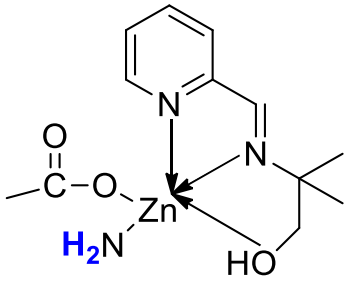


Figure 6: Probable structure after the addition of sulfide to the complex-1.

Impedance Spectroscopy for the detection of Ag^{+}:

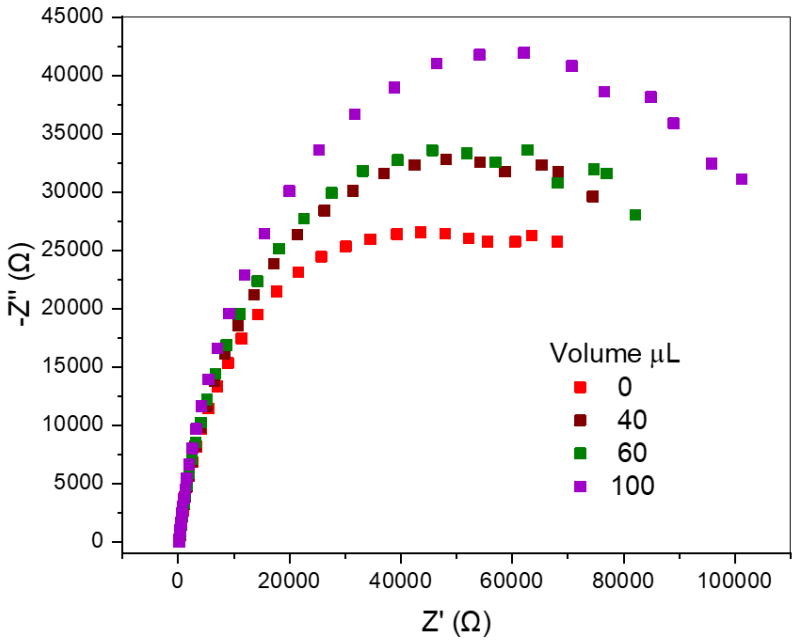


Figure7: Electrochemical Impedance spectroscopy up on addition of Ag^{+} up to 100 µl to the complex-1.

Conclusion: Herein, we have synthesised two mononuclear Zn complexes, in which complex-1 is azido complex. We have performed the sensory applications towards the both complex where we have found that only complex-1 shows high selectivity towards the detection of sulfide and Ag^{+} which has been shown by the NMR and Impedance Spectroscopy respectively.

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Chapter 5

Pyrazine assisted dimerization of oxo-bridged Schiff base Cu(II) complex.

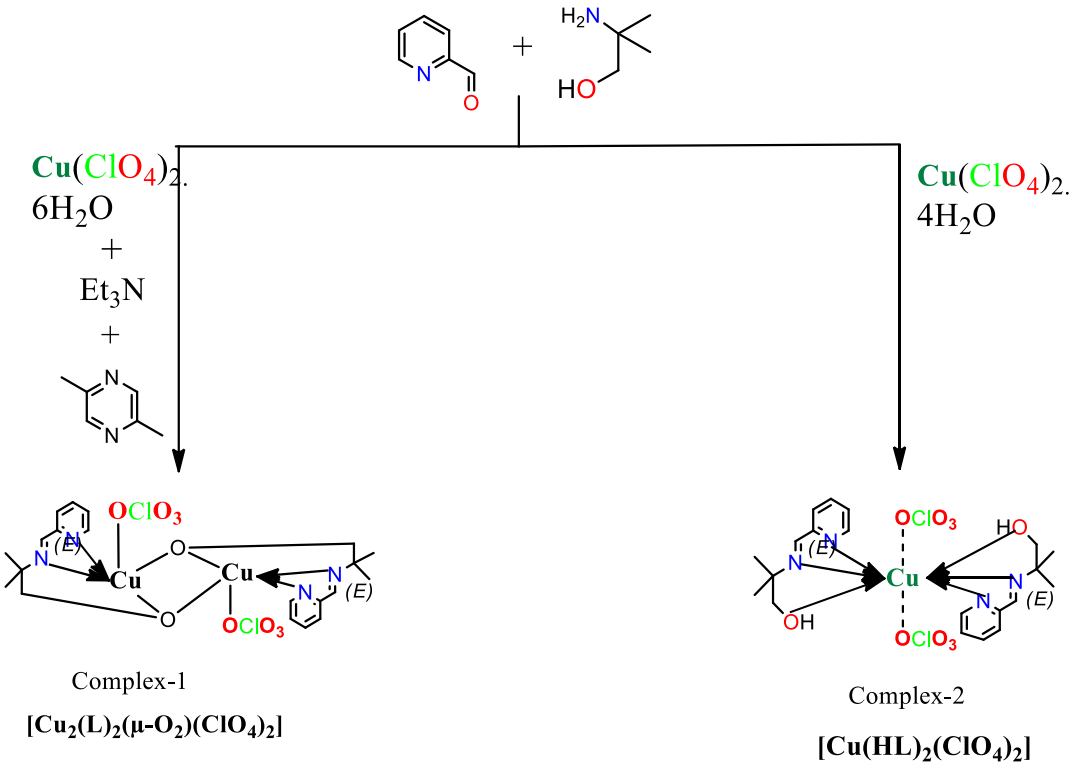
Introduction:

Schiff base Complex plays a fundamental role in catalysis, sensing, magnetism and several biological studies due to its thermal stability and reactivity. Oxo bridged complex are highly important in the catalysis and biological studies. From the biological point of view oxy-haemoglobin plays the pivotal role for the transportation of oxygen into different tissues in our body and at the same time Fe(II) in the deoxy form of haemoglobin is converted to Fe(III)-$O_2^{\cdot -}$ (super-oxo species) resulting the change of electronic and spectral behaviour of the complex. In general, from the standpoint of the Molecular Orbital diagram of the di-oxygen, it may be concluded that di-oxygen could be reduced to form super oxide, peroxide and the complete reduction upon the accepting four electrons in the anti-bonding orbital of di-oxygen results the formation of oxides. Oxo-bridged complex may transfer oxygen atom and act as an oxidizing agent. These complexes may also activate the C-H bond such as cytochrome P-450 enzyme.

Herein, we have synthesised two Schiff base complexes (Complex-1 and Complex-2) in which complex-1 forms an oxo-brideged dinuclear

complex in the presence of 2,5-dimethyl pyrazene whereas Complex-2 forms mononuclear complex.

Present work:



Results and discussions:

Synthesis:

Synthesis of $[Cu_2(L)_2(\mu\text{-}O_2)(ClO_4)_2]$ (complex-1): To 25 ml methanol 0.067g (0.63 mmol) pyridine-2-aldehyde and 0.056 g (0.63 mmol) 2-amino-2 methyl-1-propanol were stirred for half an hour in room temperature. The colour of the mixture turned colourless to light yellow. One equivalent of Et_3N (0.062g) was added followed by the addition of one equivalent of $Cu(ClO_4)_2.6H_2O$, 0.229 g (0.63 mmol) to

the reaction mixture, and the colour changed from yellow to green instantly. After 30 minutes, 0.032 g (0.31 mmol) 2,5-dimethyl pyrazine was added to it and the reaction mixture was stirred overnight. It was filtered and kept for slow evaporation. Sky blue coloured X-ray quality crystals were obtained on slow evaporation of 1:1 mixture of Methanol-n-Hexane solution. Elemental analysis calculated for the dried sample $C_{20}H_{26}N_4Cu_2Cl_2O_{12}$ resulted; found (%): C: 40.76, H: 4.83, N: 9.47; whereas cald. (%): C: 40.89; H: 4.80; N: 9.5; IR (KBr, cm^{-1}): 2981, 2056, 1586, 1440, 1353.

Synthesis of $[Cu(HL)_2(ClO_4)_2]$ (complex-2): To 25 ml methanol 0.067g (0.63 mmol) pyridine-2-aldehyde and 0.056 g (0.63 mmol) 2-amino-2 methyl-1-propanol were stirred for half an hour in room temperature. The colour of the mixture turned colourless to light yellow. One equivalent $Cu(ClO_4)_2.6H_2O$, 0.229 g (0.63 mmol) to the reaction mixture, and the colour changed from yellow to green instantly. The reaction mixture was stirred overnight. It was filtered and kept for slow evaporation. Green coloured X-ray quality crystals were obtained on slow evaporation of 1:1 mixture of Methanol-n-Hexane solution. Elemental analysis calculated for the dried sample $C_{20}H_{28}N_4CuCl_2O_{10}$ resulted; found (%): C: 40.76, H: 4.83, N: 9.47; whereas cald. (%): C: 40.89; H: 4.80; N: 9.5; IR (KBr, cm^{-1}): 2981, 2056, 1586, 1440,1353.

X-Ray crystal structure of complex-1:

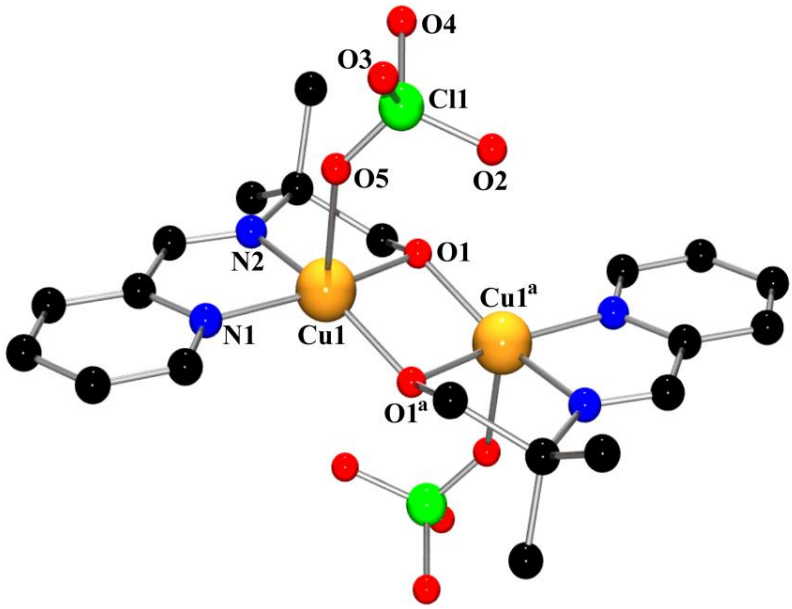


Figure 1: X-Ray crystal structure of $[Cu_2(L)_2(\mu\text{-}O_2)(ClO_4)_2]$ complex-1.

X-Ray crystal structure of complex-2:

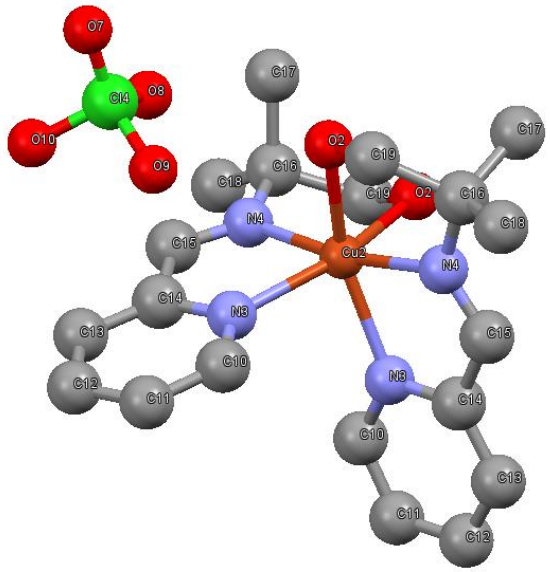


Figure 2: X-ray crystal structure of $[Cu(HL)_2(ClO_4)_2]$ (Complex 2)

Electronic spectroscopy: In order to investigate electronic property of the complex-1 and complex-2, UV-Vis was carried out

using 10^{-4} M ACN solution at room temperature. The spectrum of complex-1 in ACN medium exhibited a discrete peak at 285 nm due to the ligand-localised n-π* transition. The n-π* transition corresponds to the transition in the aromatic pyridine moiety. In addition to this, a minor contribution from low-energy transition is assigned due to ICT (Intra-ligand change transfer) overlapped with a MLCT ($M_{d\pi}$-HL_{π^*}) at 234 nm leading to the overall colouration of the metal complex-1.

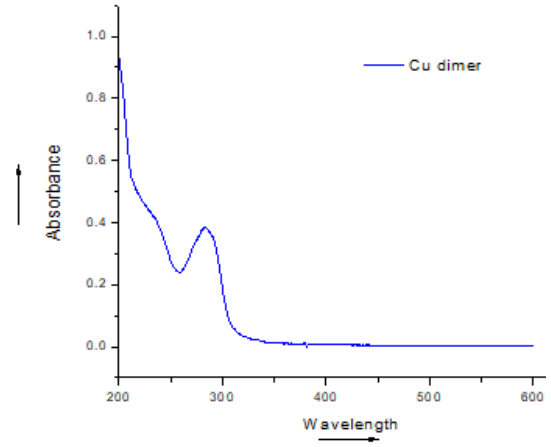


Figure 3: UV visible spectra of the complex-1 in 10^{-4} (M) ACN medium

However in case of complex-2, the n-π* and π -π* transitions were found at 282 nm and 232 nm respectively. As there is no basic difference between the complex-1 and complex-2 in terms of n-π* and π -π* transitions which are common for both the system, hence no drastic difference were observed.

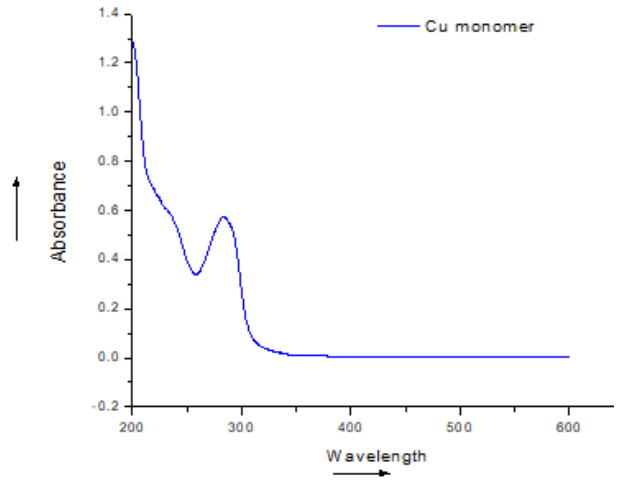


Figure 4: UV visible spectra of the complex-2 in 10^{-4} (M) ACN medium

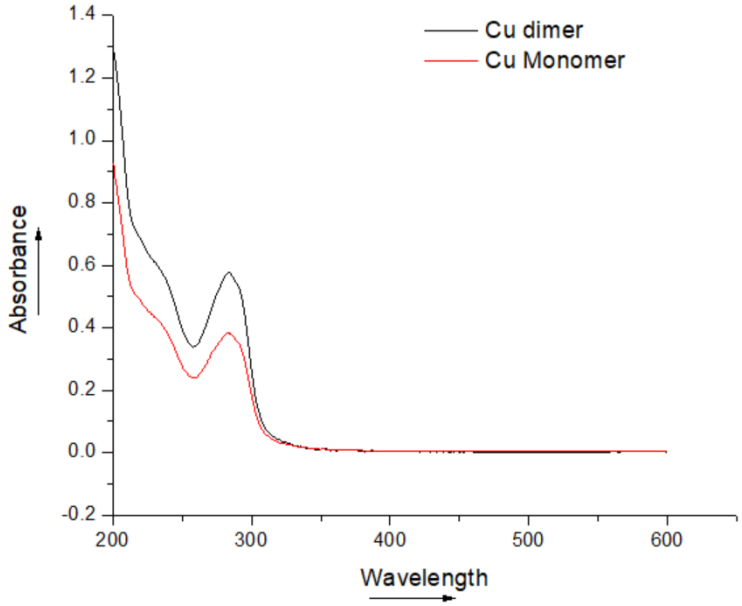


Figure 5: Stack plot of the UV-visible spectra of complex-1 and complex-2 in 10^{-4} (M) ACN

Infra-Red Spectroscopy:

FT-IR analysis of both the compounds (complex-1 and complex-2) was carried out using KBr disk. The complex-1 shows characteristics band at 1100 cm^{-1} due to perchlorate stretching, 1625 cm^{-1} due to the Schiff base formation and another bands around 3100 cm^{-1} is due to C-H stretching.

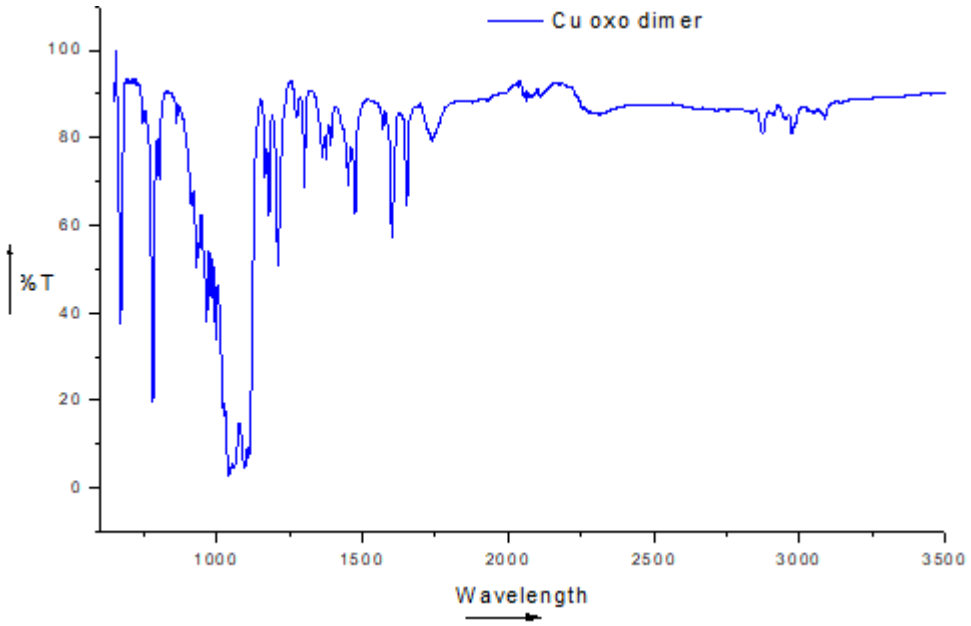


Figure 6: IR spectra of the complex-1

However in complex-2, including the above mentioned band, there is one extra band at 3350 cm^{-1} due to the intermolecular hydrogen bonding of –OH of the ligand.

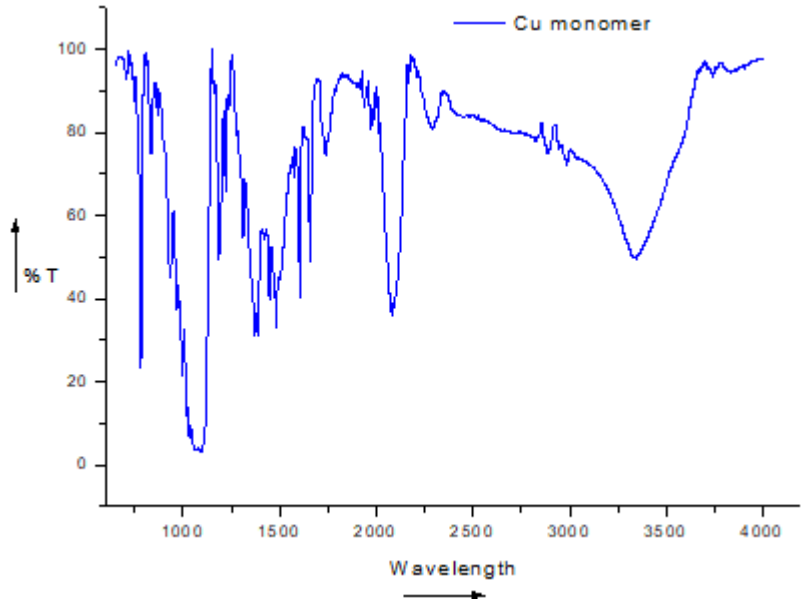


Figure 7: IR spectra of the complex-2

Chapter 6: Scope of the thesis

This thesis covers the broader section of the chemistry and the material sciences of our daily needs. To keep healthy environment, we must keep our environment free from hazardous analytes such as Hg(II), As(III), Ag(I), S^{2-} etc. Hence it is our urgent need to detect these hazardous analytes up to very low level. We have explored our study for the cheap and easy detection of Sulfide and Silver ions by Schiff base metal complexes which might be the footstep of material sciences in near future and could also be administered as a device material for the detection of hazardous analytes. Modern technology is mostly depending upon the magnetic materials. It has a huge application as data storage, hard drive, pen drive, ATM etc. Hence to use the magnetic material for these afore said application we need data storage device. We have synthesised magnetic material which could store the information. Finally we have explored on the catalysis which is the backbone of industry. We have shown catalytic application for the mimicking activity. We have discussed chapter wise briefly of my work in the following:

In the **first chapter**, I have discussed on the synthesis of mononuclear Schiff base complexes [Co(II) and Ni(II)] and studied their sensing properties towards Sulfide which is a hazardous analyte. Hydrogen Sulfide is very hazardous gas and according to the report produced by W.H.O, the toxicity of sulfide is next to cyanide toxicity on human body. Hence from this perspective, it's urgent need to detect the hazardous analytes up to very low level. We have shown that the Co(II) complex could able to detect sulfide up to nano molar range.

In the **second chapter**, I have discussed on the synthesis of azido bridged dinuclear complexes [Ni(II) and Mn(II)] and studied their sensory response towards the hazardous analytes such as Sulfide and Silver ion. It has been found that Ni(II) complex (BS-1) can detect both sulfide and Silver ion however the Mn(II) complex specifically detects only Silver ion selectively.

In the **third chapter**, I have discussed on the synthesis of three isostructural hexanuclear 3d-4f heterometallic clusters and their magnetic properties. It has been found that complex-1 and complex-2 shows ferromagnetic behaviour however the complex-3 shows anti-ferromagnetic behaviour. This molecular based magnetic material could be administered as a future data storage device.

In the **fourth** chapter, I have discussed on the synthesis of Zn-azido and Zn-perchlorato complex and studied their sensory application towards Sulfide and Silver ion. We have also shown the mechanistic approach for the sulfide detection by NMR spectroscopy as Zn(II)-complex being the NMR active species due to diamagnetic nature. We have also discussed between the structural co-relation between the Zn-azido and Zn-perchlorato complex.

In the **fifth** chapter, we have discussed on the synthesis of pyrazene assisted dimerization of the oxo bridged Cu(II)- complex . The catalytic application is yet to explore.

<u>Publication</u>:

1) Exploratory studies on azido-bridged complexes (Ni^{2+} & Mn^{2+}) as dual colorimetric chemosensors for S^{2-} and Ag^{+}: combined experimental and theoretical outcome with real field application, **Nithun Ranjan Pandit**, Sourav Bej, Ananya Mondal, Meenakshi Ghosh, George E. Kostakis, Annie K Powell, Priyabrata Banerjee and Biplab Biswas, ***Dalton Transactions***, 2020, 49, 13090-13099. (https://doi.org/10.1039/D0DT02846K).

2) Unveiling Role of Metals in Mononuclear Metal-Complexes for Chemodosimetric Detection of S^{2-} from aqueous medium: Experimental & DFT corroboration with Real-Field application. (Accepted in ***Chem Select***).

3) Recent advancement of metal-organic frameworks in sensing platform: relevance in welfare of environment and medical sciences in

line with cancer and SARS-COV-2 (under resubmission after revision in ***JMCA*)**.

National and International Conference:

- Oral presentation of the paper entitled as "Azido bridged Metal (Ni^{2+} and Mn^{2+}) as dual colorimetric ditopic chemosensor for the detection of S^{2-} and Ag^{+}" was presented in the 58th Annual Convention of Chemists, 2021 & International Conference on "***Recent trends in Chemical Sciences (RTCS-2021)***" organized by the Indian Chemical Society, Kolkata during December 21st-24th, 2021.

- Oral presentation of the paper entitled as "Exploratory studies on Azido-bridged Metal (Ni^{2+} and Mn^{2+}) clusters as ditopic Colorimetric Chemosensor for S^{2-} and Ag^{+} in 3rd International Conference on "***Chemical and Environmental Sciences (ICCAES 2021)****"* organized by Department of Basic Science and Humanities Institute of Engineering and Management, Kolkata in association with University of Engineering and Management, Smart Society, USA and Canada.

Award:

I received the **best oral presentation** award in 3rd **International Conference** on Chemical and Environmental Sciences (ICCAES 2021) organized by Department of Basic Science and Humanities Institute of Engineering and Management, Kolkata in association with University of Engineering and Management, Smart Society, USA and Canada.

Acknowledgement:

I am very grateful to my supervisor Dr. BiplabBiswas, Assistsnt Professor in Chemistry, Presidency University who has initiated this study and extended the concept with keen interest. His guidance, and constant advice and moreover his encouragement throughout the entire

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I am also thankful to all the faculty members of the Department of Chemistry, Presidency University including the authority for providing the laboratory space for this research work.

Forwarded

Signature of the candidate

Nithun Ranjan Pandit

Dr. Biplab Biswas

Supervisor

Assistant Professor of Chemistry

Presidency University, Kolkata

To,

Dr. Arnab Halder,
Associate Professor,
Head of the department,
Department of Chemistry,
Presidency University,
Kolkata 73

Respected sir,

This is for your kind attention that I, **Nithun Ranjan Pandit,** a research fellow in our university at Department of Chemistry. I have done two years of research work after my Ph.D. registration (**R-17RS205110097**), held on **10th July, 2018**, under the mentorship of **Dr. Biplab Biswas**. As per university Ph.D. guidelines, I am eligible to submit my research work as 5000-word synopsis entitled -" SYNTHESIS AND CHARACTERISATION OF METAL ORGANIC FRAMEWORK BASED ON 3d AND 4f METALS". For your kind perusal herewith I am attaching the Xerox copy of coursework mark sheets, registration certificates, conference certificates, and first pages of publications, as well as a summary write-up of my research work in 5000 words.
Hence, I kindly request you to take at the earliest best possible initiative in submitting my 5000-word synopsis.
Thanking You. Best Regards.

Nithun Ranjan Pandit

Research Scholar

Presidency University, Kolkata